SYNTHESIS OF ULTRAFINE BARIUM TITANATE CERAMIC POWDER

By

H. S. RAVISHANKAR
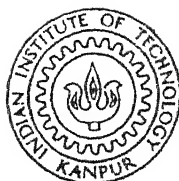
DEPARTMENT OF METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

DECEMBER, 1978

SYNTHESIS OF ULTRAFINE BARIUM TITANATE CERAMIC POWDER

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
H. S. RAVISHANKAR

to the
DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
DECEMBER, 1978

CERTIFICATE

Certified that the thesis entitled 'Synthesis of Ultrafine $BaTiO_3$ Ceramic Powder' has been carried out under my supervision and has not been submitted elsewhere for a degree.

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3.1.79

ACKNOWLEDGEMENTS

I express my indebtedness to Dr. Kailashnath Rai for having initiated me into this topic and for his excellent guidance and constant encouragement throughout the course of this work.

I am extremely grateful to Professor E.C. Subbarao for the enlightening discussions and timely suggestions. I thank Dr. S. D. Bokil for permitting me to use the facilities in Environmental Laboratory.

I thank Mr. Manohar Mungole, Mr. B. Sharma, Mr. K. P. Mukherjee, Mr. Pandey and Mr. Nayyar for their assistance at various stages of experiments.

I gratefully acknowledge the help received from all the Chemistry research scholars, especially Mr. V.V. Ramana Rao during this investigation. I owe a special debt to Hiremath without whose help this work could not have been carried out. I should make special mention of Raza, Devraj, Mukherjee, Sarkar, Chatterjee, Ghosh and B.P. who cheered me during my many journeys to different labs.

Neat drawings by Mr. V. P. Gupta and flawless typing by Mr. Nihal Ahmad is appreciated.

Finally I thank Mr. Vishwanath Singh for his excellent cyclostyling work.

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PREFACE

Conventional method of preparing $BaTiO_3$ ceramic powder has its own limitations regarding particle size and purity. To overcome this, many chemical methods have been investigated, of which metal organic route proves to be most successful.

In the literature available on synthesis of $BaTiO_3$ ceramic powder by metal alkoxide route, workers have always preferred a higher alkoxide of Ti [Eg. $Ti(OC_4H_9)_4$, $Ti(OC_5H_{11})_4$] having a lower hydrolysis rate. A previous attempt to synthesize $BaTiO_3$ by hydrolysis of a lower alkoxide like $Ti(OC_3H_7)_4$ in $Ba(OH)_2$ solution [22] resulted in a very low Ba/Ti ratio. Keeping in view this fact, an attempt was made to synthesize $BaTiO_3$ close to stoichiometry by hydrolysing the same lower alkoxide of Ti, i.e. $Ti(OC_3H_7)_4$ in a very high pH ($>$13) $Ba(OH)_2$ solution.

Moreover DTA studies made on ultrafine $BaTiO_3$ [21] does not explain the exothermic peak observed in the $400^{\circ}C$ range. Hence a detailed characterisation of the above powder was made using x-ray, chemical, DTA/TGA and Electron microscopic techniques. Sintering of these powders at relatively low temperatures compared to that required for conventional material was carried out.

In the present thesis, the first chapter deals with the literature review of the synthesis of different ceramic

oxides and multicomponent systems in the ultrafine particle.
range. Experimental details of the synthesis of $BaTiO_3$
are given in the second chapter. In the third chapter, the
results of the characterisation of the powder are given.
Studies on sintering, microstructure and dielectric proper-
ties form the fourth chapter.

Chapter 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Ultrafine Ceramic Powders

Ceramists have always been interested in obtaining high purity ultrafine ceramic powders ($<1\mu$) for the preparation of high density ceramic bodies. Since driving force for sintering comes from reduction in surface free energy, which is high for ultrafine powders because of their fine size and large surface area, such materials sinter to dense bodies almost reaching the theoretical density at substantially lower processing temperatures. Apart from this, these ceramic bodies show a great improvement in their properties when compared with those prepared by conventional methods.

It is not possible to produce very fine powders with high surface energies by usual methods like grinding. Out of the many methods described in literature for obtaining ultrafine powder, the simplest seem to be co-precipitation. This method involves dissolving the water soluble salts of the desired cations in the required proportion in hot distilled water and adding a stoichiometric amount of ammonium oxalate. This gives rise to a desired solid solution of oxalates. This is heated at a temperature

sufficient to decompose the oxalates into oxides. Schule
and Deets Creek [1] have synthesized Nickel and Cobalt
ferrites in the range 300-700 $\overset{\circ}{A}$ using this method.
Claubaugh et al. [2] have reported the synthesis of fine
Berium titanate by the above method.

The most successful method in the field of synthesis
of ultrafine ceramic powders involves the use of organo-
metallic compounds. The preparation of ceramic fine
powders using metal organic compounds such as metal alkoxides,
not only gives ultrafine particle size, but also gives a
product in which the constituents have been mixed at
molecular levels. Doping and stabilizing of ceramic material
has been extremely successful in this method. Yoldas [3]
has listed the attractive properties of materials synthesized
by the method as follows:

1. High purity
2. Molecular homogeneity
3. Submicron particle size
4. High reactivity
5. Low processing temperature.

1.2 Metal Organic Compounds as Ceramic Precursors

As the name implies, metal organic compounds consist
of compounds having organic groups attached with a metal.
Metal alkoxides with general formula $M(OR)_n$ where M is the

metal and R, the organic group (Eg. C_3H_7, C_4H_9 etc.).
Alkoxides of metals can be synthesized easily and they can
be converted into metal oxides either by thermal degrada-
tion or hydrolyzation followed by dehyaration.

$$M(OR)_n \xrightarrow{\text{Thermal degradation}} MO_{n/2} + n/2 \ ROH + \text{Olefins} \tag{1}$$

$$M(OR)_n \xrightarrow{\text{Hydrolysation}} M(OH)_n + n \ ROH \tag{2a}$$

$$M(OH)_n \xrightarrow{\text{dehyaration}} MO_{n/2} + n/2 \ H_2O \tag{2b}$$
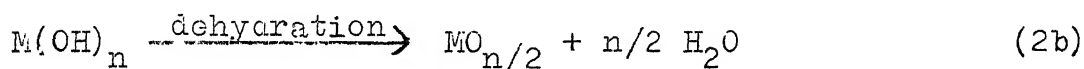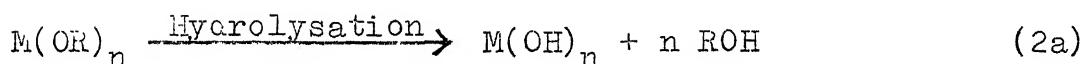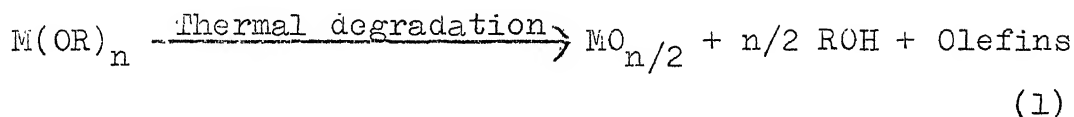
Generally the above reactions take place below $500^\circ C$ and
the product consists of unusually small particles of size
typically around 100 Å.

1.2.1 Synthesis of ultrafine ceramic oxides from metal alkoxides

Metal alkoxides are most useful compounds for the
ceramic forming processes, especially in the case of group
III and group IV metals. The oxides of these metals
constitute a large portion of ceramic compositions and
alkoxides of these metals can be synthesized very easily.
Chemical synthesis of some important oxides are given below.

(a) Alumina : Alkoxides of aluminum can be obtained by the
method first developed by Adkins [4]. In presence of
mercuric chloride, aluminum and isopropyl alcohol react to

give aluminum isopropoxide. 4 hours of refluxing is necessary for complete reaction to take place. These alkoxides can be decomposed (around $500^{\circ}C$) or hydrolyzed to get fine alumina.

Higher alkoxides of aluminum can be obtained by ester exchange reaction developed by Mehrotra [5] in which aluminum isopropoxide is mixed with the desired higher alcohols and benzene and refluxed after which isopropyl alcohol is removed by distillation of alcohol--benzene azeotrope. Ester exchange reaction can be represented by the following equation,

$$M(OR)_n + R'OH \xrightarrow{\text{reflux}} M(OR')_n + ROH \qquad (3)$$
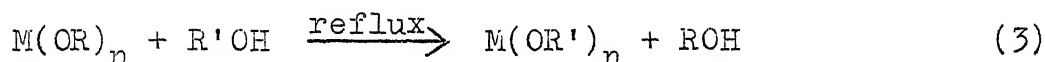
where M is the metal, R the organic group and R' the heavier organic group which replaces R.

(b) <u>Zirconia, Titania and Hafnia</u> : The alkoxides of zirconium, Titanium, Hafnium can be synthesized by the method of Bradley et al [6]. The reaction in general for all the three metal alkoxides can be represented by the following equation,

$$MCl_4 + 4C_3H_7OH + 4NH_3 \xrightarrow[C_6H_6]{5^{\circ}C} M(OC_3H_7)_4 + 4NH_4Cl \qquad (4)$$
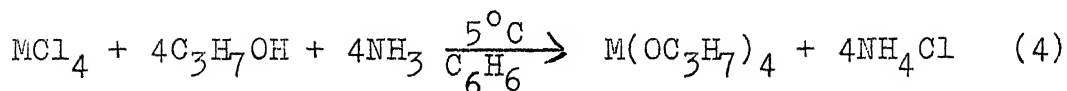
External cooling is necessary as the reaction is exothermic. The higher alkoxides of these metals can also be synthesized using the ester exchange reaction mentioned earlier. Thermal degradation or hydrolyzation followed by dehydration

of these alkoxides give fine oxide powders in the range
100 Å - 200 Å. Thermal degradation of these alkoxides
involve two steps as determined by DTA [7]. The first step
involves removal of bound alcohol and around $400^{\circ}C$, oxide
formation is complete.

(c) <u>Rare Earth metal oxides</u> : Rare earth oxides have
received much attention due to their application in nuclear,
electronic, laser, optical and phosphor materials [8].
Classical method of alkoxide synthesis fail to give rare
earth alkoxides in a pure form. The reason for this is
given briefly below.

Rate of reaction for preparation of alkoxides are
faster for compounds having small covalent radii. Covalent
radii of Al, Li, Ti are 1.25 Å, 1.23 Å, 1.32 Å and the
reactions are relatively rapid. For Zr and Hf, it is 1.45Å
and 1.44Å and reactions are considerably slower. For Y,
Yb, Dy (Atomic radii 1.62 Å, 1.59 Å, 1.7 Å) the reactions
are much slower and it is hard to drive the reaction to
completion. Mazdiyasani and Lynch [9] synthesized Y, Dy
and Yb alkoxides using a reaction employed by Adkins[4]
for the synthesis of Aluminum isopropoxide. The reaction
can be represented as below,

$$M + HgCl_2 + 3ROH \xrightarrow{82^{\circ}C} M(OR)_3 + Hg + 2HCl + \tfrac{1}{2}H_2 \quad (5)$$
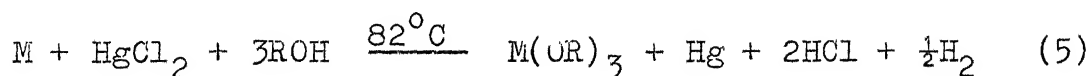
where M is Al, Y, Dy and Yb and R is the isopropyl group.
For rare earths a minimum 24 hours refluxing is necessary

for the reaction to be completed. 10^{-3} to 10^{-4} mole of $HgCl_2$ is sufficient to act as catalyst. The mercury formed during the reaction, combines with M to form an amalgum.

$$M + Hg \longrightarrow M(Hg) \tag{6}$$

$$M(Hg) + 3ROH \longrightarrow M(OR)_3 + Hg + \frac{3}{2}H_2 \tag{7}$$
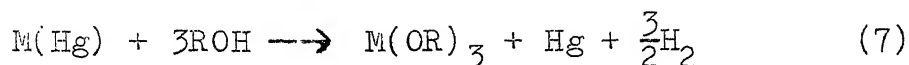
For lower lanthanides, namely La, Ce, Nd and Pr, a mixture of $HgCl_2$, $Hg(C_2H_3O_2)_2$ or HgI_2 is used to increase both the rate of reaction and also percentage of yield [10].

These alkoxides, on thermal degradation or hydrolytic decomposition give fine particles of rare earth oxides in range 100 $\overset{o}{A}$-200$\overset{o}{A}$.

1.2.2 Synthesis of multicomponent systems :

The utility of organometallic route is well illustrated in the synthesis of multicomponent systems.

Control of stoichiometry, impurity level, porosity and grain size are important in obtaining poly crystalline ternary and quartenary electronic ceramic bodies which transmit incident light. Hot pressing is the general method used for processing such materials. Mazdiyasani and Brown [11] have developed dense, transparent PLZT bodies by ordinary cold pressing and sintering at temperature as low as $1150^{o}C$, using PLZT powder synthesized from alkoxides. Zr, Ti and La alkoxides were prepared according to the eqns. 4 and 5. Lead alkoxide was prepared by reacting sodium alkoxide with

lead acetate. The mixture of all the four alkoxides in proper proportion were mixed in a common solvent like benzene and hydrolyzed. The resulting hydroxide on drying gives PLZT powder.

Conventional method of stabilizing Zirconia with Yttria in cubic phase requires at least 8 mole percent yttria and temperature of the order of $2000^{\circ}C$. But from organometallic route Mazdiyasani, Lynch and Smith [12] have found that 6 mole percent of yttria is sufficient to stabilize zirconia at temperature as low as $850^{\circ}C$.

Mullite $(3Al_2O_3 \cdot 2SiO_2)$ has been synthesized by Mazdiyasani and Brown [13] using organometallic route. Aluminum alkoxide was synthesized by Adkin's method [4]. Silicon alkoxide was prepared as below,

$$SiCl_4 + 4\ C_3H_7OH \xrightarrow{82^{\circ}C} Si(OC_3H_7)_4 + 4HCl \qquad (8)$$
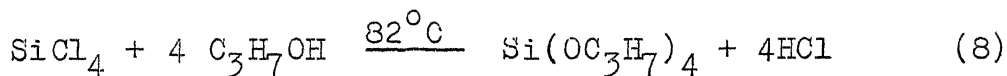
Mixture of these alkoxides in proper quantity were hydrolysed and then dried to get fine mullite particles. All these as synthesized materials will be amorphous and on calcination at a moderate temperature ($700^{\circ}C$-$800^{\circ}C$) give fine crystalline material. The governing factor in the above methods is that alkoxides involvedmust have relatively compatible reaction rates.

1.3 Synthesis of BaTiO$_3$ Ceramics

Titanate ceramic bodies have been largely used in electronic component industry and newer trends in electronics

are requiring greater sophistication in all components including capacitors. Higher reliability, lower aging rates, greater frequency and voltage independence as well as higher dielectric constant, higher dielectric strength and reduced temperature dependence are the properties being sought in capacitors. Initial material play a great role in the improvement of these ceramic bodies [14] and it is worthwhile to look into the different methods of preparing this.

1.3.1 Limitations of commercial method

In the commercial method of preparing $BaTiO_3$, the ingredients $BaCO_3$ and TiO_2 are blended together and fed to a calciner, typically a gas fired **rotary** kiln. The calcined product in the form of hard to soft clinkers are ball milled to get fine particles and then dried. There are number of difficulties which set limitations on quality control like (a) quality and particle size of incoming ingredients, (b) contamination from kiln gas and kiln lining and (c) ball milling media. A compromise that may have to be struck between hardness and calcining vs milling time to maintain both low silica content and low particle size also affects the quality of the final product. The seriousness of the effect of contamination during grinding on the final properties of material has been studied by Nelson and Cook [15]. Wet milling is the general process employed in

the preparation of $BaTiO_3$ ceramics. Typical chemical analysis of commercially pure $BaTiO_3$ contains 0.5% SiO_2 and 0.25% Al_2O_3 introduced mostly during milling. Nelson and Cook found that the dielectric constant of the material decreased to 35%, of the original value when it was ground in alumina medium for 12 hrs and to 65% of original value when ground in porcelein medium for same duration.

Besides chemical problem, there are physical problems which greatly influence the ultimate properties of a fired ceramic. The calcined product must be comminuted to achieve a small particle size. The particle sizes of even 1μ-5μ are not as good as one would desire for optimum sintering.

Analysing the above factors Hyatt and Laird [14] have proposed following improvement in the initial material.

1. ABO_3 stoichiometric accurate to 99.5% with A/B ratio 1 ± 0.005

2. SiO_2, Al_2O_3, Na_2O, K_2O < 0.05%

3. SrO < 0.5%

4. Intimate mixing or coprecipitation.

Hyatt et al. [16] have conducted an experiment to show the effect of initial material on final sintering. Sintering studies were conducted on five materials from different sources. Four of these were 99% pure and had a particle size in the range 0.05μ-0.5μ and the fifth one, a commercially

pure (CP) grade material with 97.5% purity and particle size 0.5μ-3μ. They found that submicron size material gave high density and low porosity in the range 1260°C-1320°C whereas CP grade material did not mature below 1400°C.

1.3.2 Synthesis of BaTiO$_3$ ceramics by oxalate technique

Considering the limitations of the conventional methods, several new methods have been investigated to get high purity ultrafine BaTiO$_3$ ceramics. Claubaugh et al.[17] have developed fine, stoichiometric BaTiO$_3$ by decomposition of double oxalate of Barium and Titanium (BaC$_2$O$_4$·TiO(C$_2$O$_4$)· xH$_2$O). An aqueous solution containing TiCl$_4$ and BaCl$_2$ in which the two compounds are in nearly equimolar proportion, but with Ba in slight excess is slowly added to a hot solution of oxalic acid containing about 10% more of acid than required for the desired double oxalate. On ignition, this double oxalate gives fine BaTiO$_3$ with Ba/Ti ratio of 1 ± 0.001.

1.3.3 Synthesis of BaTiO$_3$ from organometallic compounds

Mazdiyasani [18] has synthesized high purity stoichiometric ultrafine BaTiO$_3$ by hydrolysis of alkoxides. Barium isopropoxide was synthesized by the reaction

$$Ba + 2\ C_3H_7OH \xrightarrow{\ 82°C\ } Ba(OC_3H_7)_2 + H_2 \qquad (9)$$
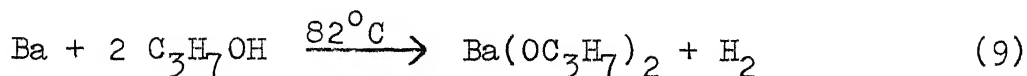
Titanium isopropoxide was synthesized as described earlier (Eq. No. 4) and converted to Ti(OC$_5$H$_{11}$)$_4$ by ester exchange

reaction. These two alkoxides taken in proper ratio were dissolved in a mutual solvent like benzene and after refluxing for two 2 hrs, hydrolyzed to get $BaTiO_3$ precipitate.

$$Ba(OC_3H_7)_2 + Ti(OC_5H_{11})_4 + 3H_2O \xrightarrow{\text{exothermic}} BaTiO_3 + 2C_3H_7OH + 4C_5H_{11}OH \quad (10)$$
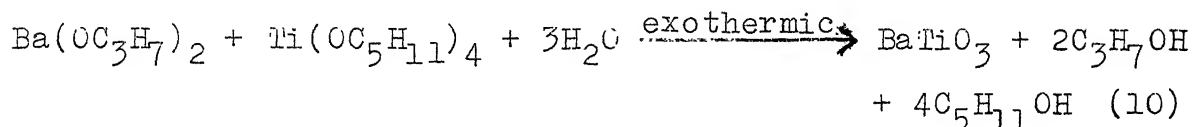
The reaction was carried out in CO_2 free atmosphere. The precipitate after drying consisted of fine particles in the range $50\text{Å}-100\text{Å}$ and after calcination at $700^{\circ}C$ for 60 minutes they grew to 300 Å and 80% of the particles were less than 350Å. Emission spectrographic analysis showed progressive decrease in impurities level at every step and the final product was 99.98% pure. Sintering at $1300^{\circ}C$ for one hour gave densities close to theoretical value.

Synthesis of $BaTiO_3$ from citrate is also mentioned in literature. But details regarding this are not available.

1.3.4 Synthesis of $BaTiO_3$ by hydrolysis of Titanium alkoxide in $Ba(OH)_2$ solution

Synthesis of $BaTiO_3$ ceramic powder by addition of titanium alkoxides to a highly alkaline $Ba(OH)_2$ solution was first reported by Flaschen [19]. Nelson [20] has developed a model to explain the above mechanism. This will be taken in detail in next chapter. Ern [21] has studied DTA of $BaTiO_3$ synthesized by this method (Ba/Ti ratio 1.03). Following is the result of his experiment. Two endothermic peaks

at 140°C and 250°C were attributed to the dehydration of
colloidal powder. An exothermic peak at 430°C, which was
insensitive to the different atmospheres used was left as
unexplainable. A double exothermic peak at 730°C and 840°C
was assigned for the nucleation of a new phase (nucleation
of small amount of BaO from loosely crystalline $BaTiO_3$).

Kiss et al. [22] have studied in detail the effect of
various parameters on the product of synthesis. They found
that high pH (>12) and temperature above 30°C was necessary
to get crystalline powder. Moreover they report that
because of its high hydrolysis rate, Titanium isopropoxide
is not suitable for getting stoichiometric $BaTiO_3$ and suggest
that chelates of Titanium isopropoxide having lower hydro-
lysis rate gives more stoichiometric product.

Chapter 2

SYNTHESIS OF ULTRAFINE BaTiO$_3$ POWDER

Abstract : In the present chapter, details of the experiments conducted to synthesize ultrafine BaTiO$_3$ powder are given. The results have been discussed on the basis of a model developed by Nelson [20].

2.1 Synthesis of Titanium Isopropoxide

Titanium isopropoxide is a metal alkoxide having a freezing point of 20°C and a boiling point of 230°C. This reacts rapidly with water to form alkyl alkoxides. This can be represented by the following equation [7],

$$M(OR)_4 + H_2O \longrightarrow MO(OR)_2 + 2ROH \qquad (11a)$$

$$2Mo(OR)_2 \longrightarrow M(OR)_4 + MO_2 \qquad (11b)$$
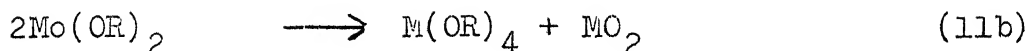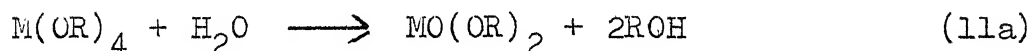
where M is Ti, Zr, Hf, Th, Y, Dy, Yb.

Apparatus : In the present experiment, glass apparatus fitted with standard interchangeable joints were used. They were scrupulously cleaned and completely dried in an oven. Extreme care was taken to exclude moisture from the apparatus.

Chemicals: 99.5% pure $TiCl_4$ supplied by Riedel De Häenag was used without any further purification. Analytical grade benzene (BDH, Bombay) was distilled after drying over sodium wire for 12 hours and this was used throughout the course of experiments. Analytical grade isopropyl alcohol (BDH, Bombay) was also used without any further purification.

Since ammonia cylinder was not available, the following method was used to obtain continuous supply of ammonia required for the experiment. Concentrated analytical grade ammonia solution was taken in a 500 ml conical flask. A few boiling chips were added to this. This was tightly fitted with a cork with a central outlet which was connected to a gas passing adopter through a rubber tubing. This ammonia solution was warmed over a low heat. A heater connected with a dimmerstat was used for this purpose. After a while ammonia starts getting liberated from the solution slowly. This gas was used for the experiments conducted. However, care was taken not to boil the solution and fresh solution was used for each experiment.

The set up used for the synthesis of Titanium iso-propoxide is shown in fig. (1).

5 ml of isopropyl alcohol and 10 ml of benzene were transferred to a 50 ml, 3 neck flask. All the three necks were closed air tight with standard stoppers using vacuum grease. This was transferred to bath containing ice and
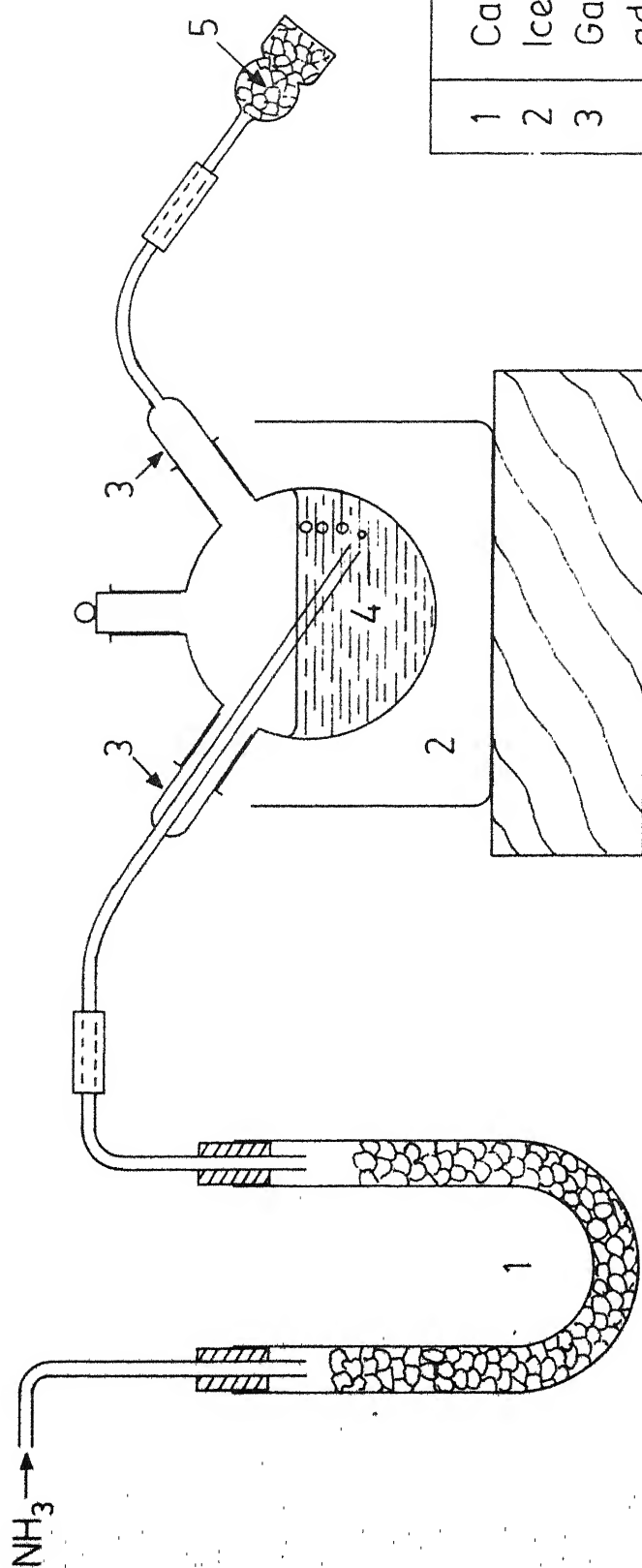
1	CaO tube
2	Ice bath
3	Gas passing adopters
4	Reaction mixture
5	CaCl$_2$

FIG. 1 SET UP FOR THE SYNTHESIS OF TITANIUM ISO PROPOXIDE

NH$_3$

salt mixture and the whole set up was transferred to a fume
cupboard. [Transfer of $TiCl_4$ from the bottle into the flask
needs this step as $TiCl_4$ which is highly sensitive to
moisture in the air gives copious fumes when the bottle
is opened.] 1 ml of $TiCl_4$ was pippetted into the flask with
the help of a pippette filter. Ammonia that is getting
liberated from the warmed ammonia solution is passed through
a U tube a freshly roasted time to make it anhydrous and
this was bubbled slowly through the reaction mixture in the
flask, using a gas passing adopter. Another gas passing
adopter was connected to the third neck and the other end
of the same was connected to a loosely filled $CaCl_2$ tube.
The second neck was kept closed all the time except while
adding the solvents.

As ammonia bubbles through the clear reaction mixture,
NH_4Cl starts getting precipitated slowly according to the
reaction,

$$TiCl_4 + 4C_3H_7OH \xrightarrow[C_6H_6]{5^\circ C} Ti(OC_3H_7)_4 + 4NH_4Cl$$
$$+ 4\ NH_3$$
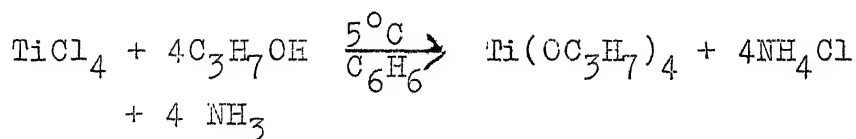
and the clear solution turns white and turbid. 20 ml of
additional benzene was added to reduce this gel like
consistency. Passing of ammonia was continued till all
the NH_4Cl got precipitated and the gas bubbled through
the clear liquid above. In the present experiment with
slow bubbling of ammonia through the reaction mixture, the

reaction was completed in 12-15 minutes. After this, the gas adopters were removed and replaced by standard stoppers. The flask was allowed to come to room temperature. During the course of the experiment this was found to be an important factor, because with the immediate removal of NH_4Cl from product, there is a chance of $Ti(OC_3H_7)_4$ also getting filtered along with NH_4Cl as it has a freezing point of $20^\circ C$.

NH_4Cl was separated from the mixture of $Ti(OC_3H_7)_4$ and the solvents by centrifuging in a centrifuge (Sorval) at 5000 rpm for five minutes. The clear liquid containing the product, traces of isopropyl alcohol and benzene was transferred to a 100 ml round bottommed flask, fitted with a standard neck. Benzene and traces of isopropyl alcohol were removed from the product by distillation under reduced pressure (5 mm). A trap immersed in liquid nitrogen was connected between the pump and the flask. The colourless $Ti(OC_3H_7)_4$ liquid remaining in the flask was used for the synthesis of $BaTiO_3$ without further purification. The yield of $Ti(OC_3H_7)_4$ product was found to be always ~~found to be~~ between 70-75% in all the experiments.

Infrared spectra of the synthesized $Ti(OC_3H_7)_4$ was taken with a Perkin-21 spectrometer and compared with the standard IR pattern [23]. The wave numbers observed are compared with the standard values in table 1. The region

Table 1

Infrared absorption data of Titanium isopropoxide
(IR absorption frequencies in cm^{-1})

Data from Bell et al.[23]	Present data
2959	(a)
2924	(a)
2851	(a)
1462	1470
1451	–
1425	–
1391	1390
1381	1385
1370	1370
1328	1330
1248	1250
1158	1160
1136	–
1124	1120
1000	1000
954	950
852	850

(a) An absorption band was observed between 2850-
3000 cm^{-1} range and individual peaks could not
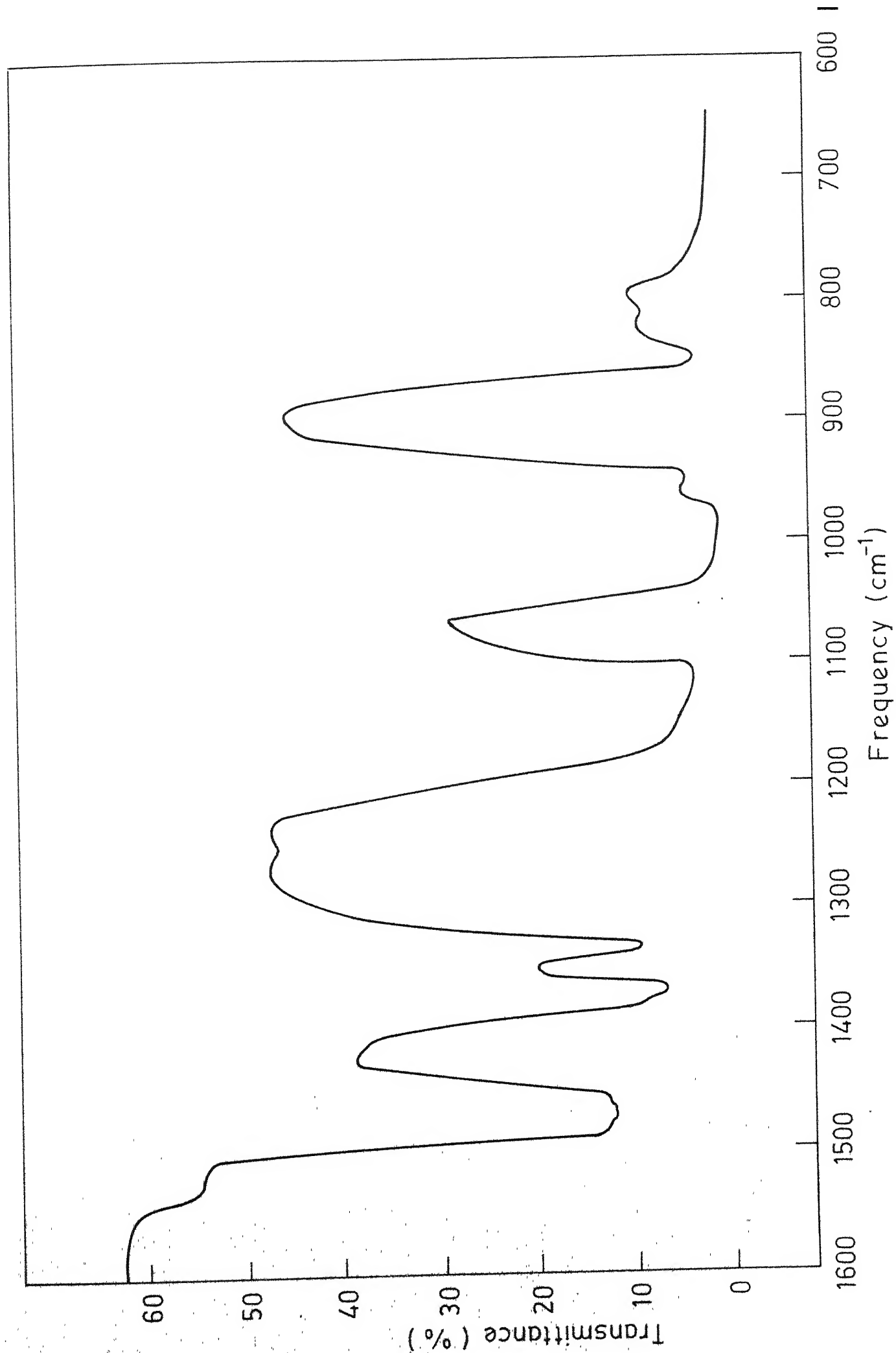be correctly observed because of suppression of
scale in this region.

Fig. 2 Infrared absorption spectrum of Ti(OC$_3$H$_7$)$_4$

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of the IR spectrum in the range 800-1600 cm^{-1} which repre-
sents the most characteristics absorption peaks of the
compound are given in the fig. (2). It can be noticed that
the observed values are matching quite well with the
standard pattern. Because of low resolution in low wave-
length region, the peaks in the range 2959 to 2857 cm^{-1}
were observed as a broad band.

2.2 Synthesis of BaTiO$_3$: The set up for the synthesis of

BaTiO$_3$ is as shown in the fig. 3. 4 gms of analytical grade
Barium hydroxide was dissolved in 20 ml of boiling double
distilled water. This solution was filtered hot to remove
any traces of Barium carbonate. The pH of this solution
was measured using Systronic pH meter and was found to be
13.2. This solution was transferred to a 100 ml 3 neck
flask and this was slowly heated in an oil bath so that the
temperature of the solution in the flask was between 85°C-
90°C. At this stage purified nitrogen was passed through
the flask using gas adopters so that nitrogen atmosphere
was maintained in the flask.

Nitrogen from the cylinder was purified as follows.
First, the gas from the cylinder was bubbled through two
traps containing a solution for absorbing oxygen. This
solution was prepared by dissolving 20 gms of KOH, 18 gms
of sodium di thionate and 1.8 gm of Naphthalene sodium

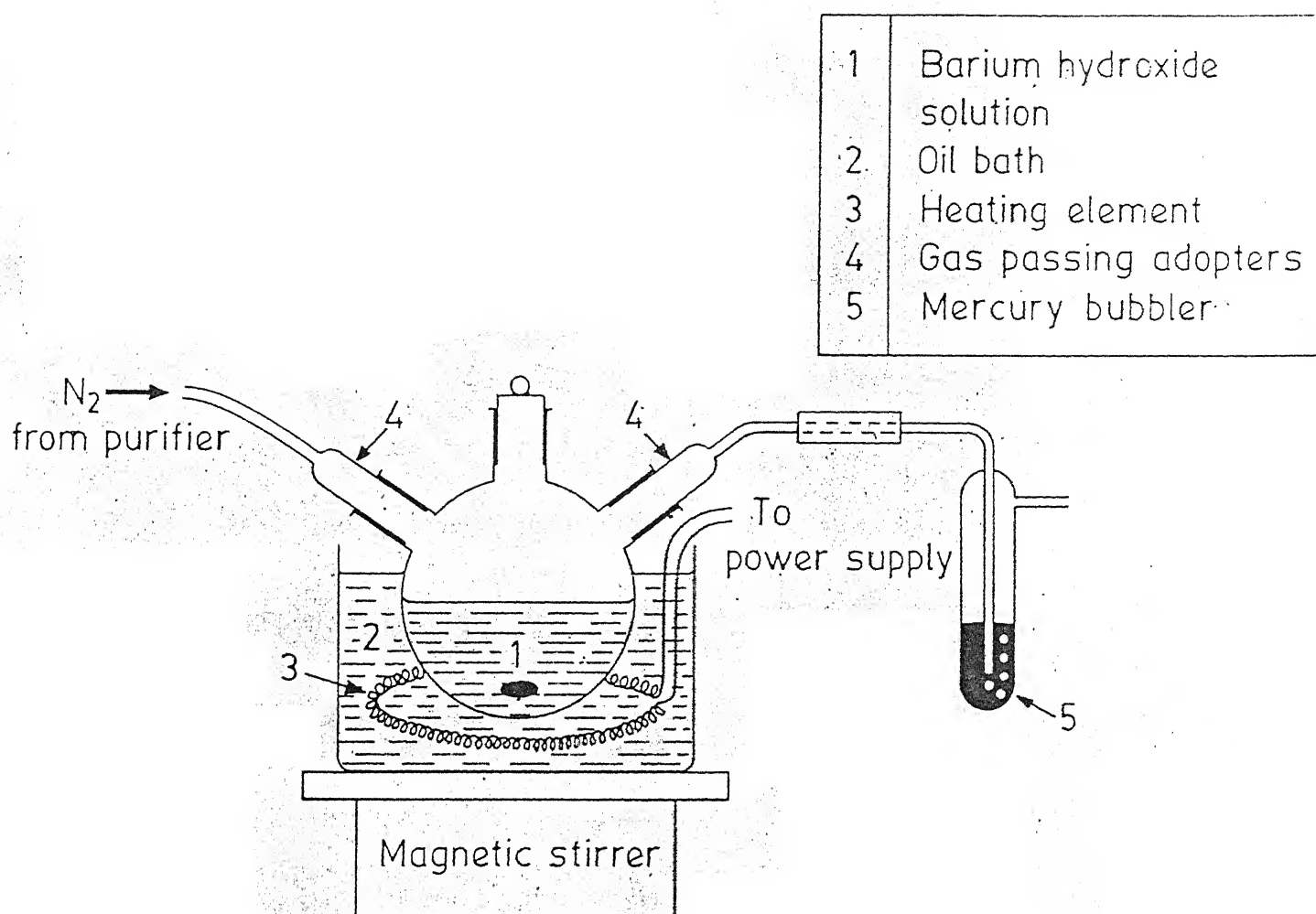| 1 | Barium hydroxide solution |
2	Oil bath
3	Heating element
4	Gas passing adopters
5	Mercury bubbler

FIG. 3   SET UP FOR THE SYNTHESIS OF BARIUM TITANATE

sulphonate in 100 ml of distilled water. After the removal of oxygen, the gas was passed through a concentrated sulphuric acid trap for the removal of moisture and finally through a KOH tower for removal of CO_2. The nitrogen gas coming out of this trap is sufficiently pure and this was used to maintain an inert atmosphere over hot $Ba(OH)_2$ solution. The solution was stirred vigorously over a magnetic stirrer.

2 cc of $Ti(OC_3H_7)_4$ was added to the vigorously stirred hot $Ba(OH)_2$ solution from a glass dropper. Care was taken to add this dropwise and also as quickly as possible. This addition instantaneously results in precipitation of $BaTiO_3$. Stirring was continued for another 10 minutes to ensure complete reaction. An atmosphere of N_2 was maintained above the solution all the time. This precaution is necessary to avoid any formation of $BaCO_3$ from $Ba(OH)_2$ which has a high affinity for absorbing CO_2. The $BaTiO_3$ precipitated was washed 8-10 times with hot distilled water to ensure removal of all excess Barium and finally this precipitate was dried in an oven at $50^{\circ}C$.

$Ti(OC_3H_7)_4$ was diluted with isopropyl alcohol to get four solutions having the concentration of alcohol as 0%, 25%, 50% and 90% by volume. $BaTiO_3$ was synthesized using all these four solutions. Following notations will be observed to indicate $BaTiO_3$ synthesized from these four

~~solutions.~~ Following notations will be observed to indicate $BaTiO_3$ synthesized from these four solutions. E.g. 25%, $50^{\circ}C$ sample refers to $BaTiO_3$ prepared using $Ti(OC_3H_7)_4$ containing 25% isopropyl alcohol and finally dried at $50^{\circ}C$, 0% $800^{\circ}C$ sample refers to a $BaTiO_3$ sample synthesized with undiluted $Ti(OC_3H_7)_4$, dried at $50^{\circ}C$ and calcined at $800^{\circ}C$.

2.3 Mechanism of Synthesis of $BaTiO_3$

Kiss et al [22] have investigated the effect of various parameters like temperature, pH and addition rate on the Ba/Ti ratio of the final product. They observed that Ba/Ti ratio was 0.42 at $30^{\circ}C$, whereas it was 1.03 at $85-90^{\circ}C$. They also found that highly alkaline $Ba(OH)_2$ solution (pH $>$ 11) was necessary to produce stoichiometric product and lower pH solution gave only acedic $BaTiO_3$ containing excess TiO_2. Another factor that was observed by them was the effect of rate of addition of $Ti(OC_3H_7)_4$ on the stoichiometry. They found that with faster addition of $Ti(OC_3H_7)_4$ the product was closer to stoichiometry.

Because of these effects, the controlling parameters of the synthesis were set as follows with the aim of achieving a product having a Ba/Ti ratio close to 1.

Temperature	$85^{\circ}C-90^{\circ}C$
Stirring	Vigorous
Addition rate	dropwise and fast
pH	13.

Nelson [20] attempted to explain the mechanism of the above synthesis. His model for the initial step when a pH of 11-14 is maintained is shown in fig. 4(a). Four molecules of water and two hydroxyl groups attach through their oxygen atoms to the titanium of $Ti(OR)_4$ in a nucleophilic reaction. One proton from each water molecule interacts with one oxygen atom of the alkoxide group through hydrogen bonding. Following an electron rearrangement, four molecules of alcohol are expelled. This results in an anion $Ti(OH)_6^{2-}$ which is neutralised by Ba^{2+} ions in the solution.

$$Ti(OR)_4 + 4H_2O + Ba^{++} + 2(OH)^- \xrightarrow{85^\circ C-90^\circ C}$$
$$Ti(OH)_6^{2-} + Ba^{++} + 4ROH \xrightarrow{-3H_2O} BaTiO_3 + 4ROH. \qquad (12)$$
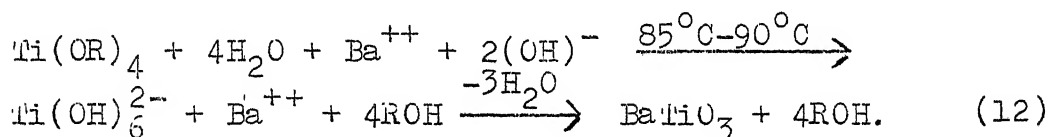
It can be considered as an acid base reaction.

This acid base reaction cannot take place in a neutral solution. The anion formation cannot take place for the lack of $(OH)^-$ ions. This results in hydrous TiO_2 without any participation from Ba^{++} ions. It shows that presence of Ba^{++} and $(OH)^-$ ions are essential for the formation of Barium titanate.

When $Ti(OC_3H_7)_4$ is added to $Ba(OH)_2$ solution, there is a local lowering of pH due to rapid consumption of $(OH)^-$ ions. Thus any factor that reduces pH, helps in the formation of acedic titanate. By vigorous stirring, distribution of $(OH)^-$ can be made uniform throughout so that there is no chance of free TiO_2 precipitating.
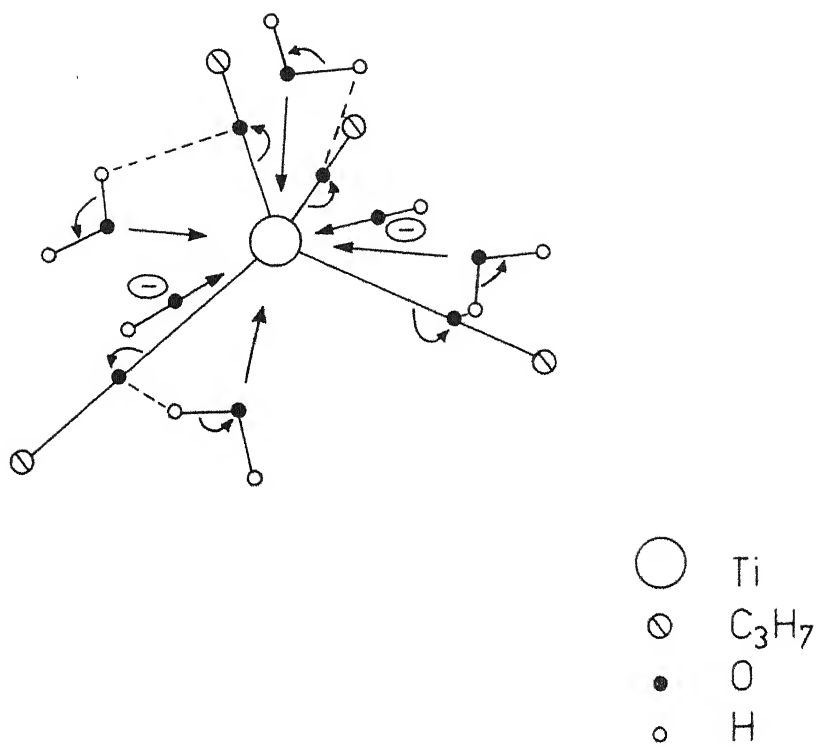
Fig. 4a   Nucleophilic attack by H_2O and OH^- on $Ti(OC_3H_7)_4$.[20]

Prolonged addition of $Ti(OC_3H_7)_4$ also causes the formation of acedic titanates. Fresh $BaTiO_3$ precipitate is highly adsorptive and a polar adsorption of Ba^{++} on freshly formed $BaTiO_3$ takes place which in turn holds a diffuse layer of $(OH)^-$ ions [Fig. 4(b)] by electrostatic forces. Because of this, availability of $(OH)^-$ ions required for the initial step of the reaction may be less compared to freely moving $(OH)^-$ ions. This may hamper the formation of $Ti(OH)_6^{2-}$ ions which are necessary for $BaTiO_3$ nucleation and may result in the formation of acedic titanate. Hence a rapid, but dropwise addition is favourable for stoichiometric product.

With increasing dilution of $Ti(OC_3H_7)_4$ particle size of $BaTiO_3$ is expected to be reduced as simultaneous formation of large number of nuclei in a short time exhausts the solution with respect to $BaTiO_3$ and hence growth of $BaTiO_3$ particle is decreased.
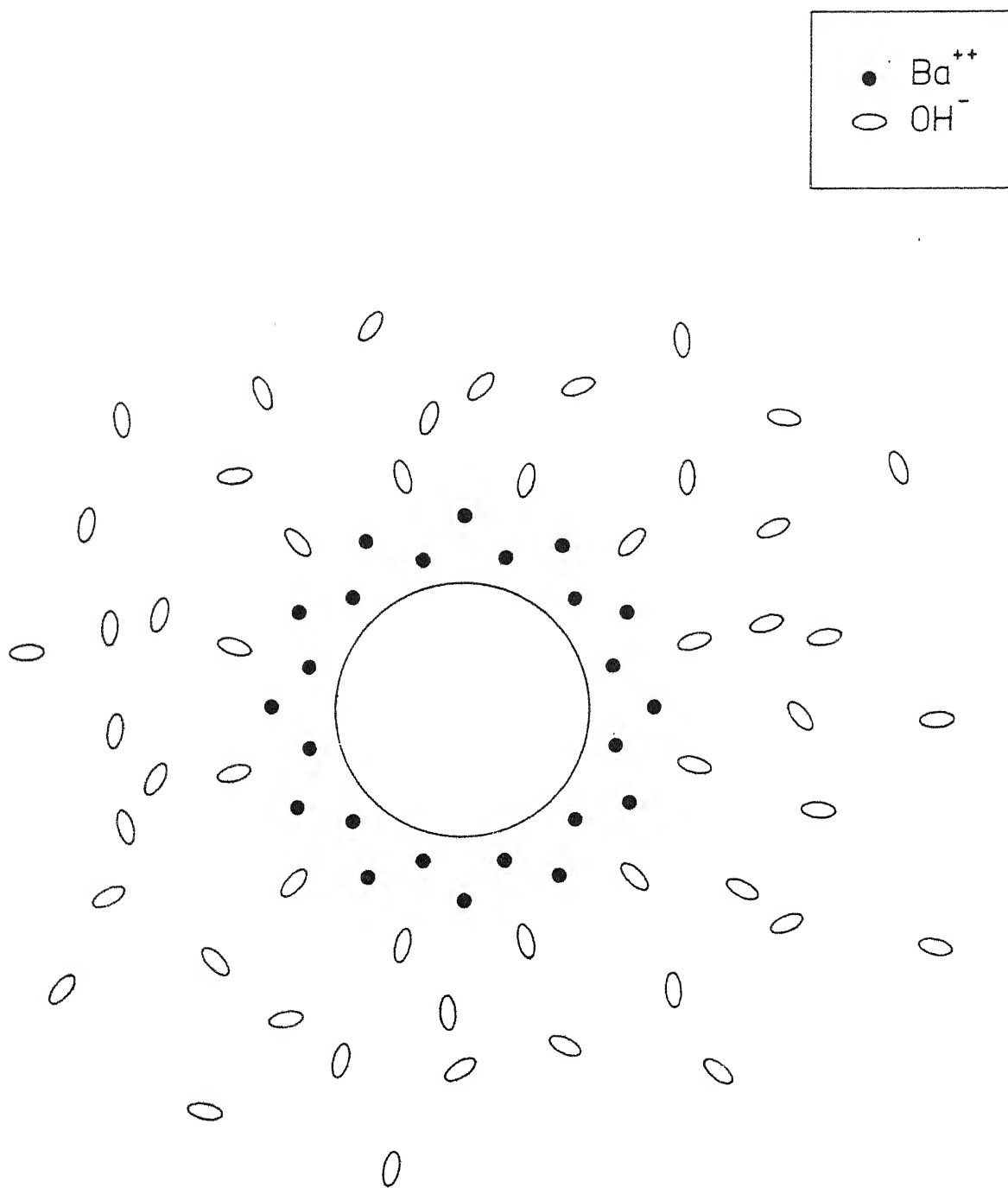
Fig. 4b   Colloidal BaTiO$_3$ micelle with diffuse layer of
          hydroxyl ions[22].

Chapter 3

CHARACTERISATION OF ULTRAFINE $BaTiO_3$ CERAMIC POWDER

Abstract : $BaTiO_3$ powder synthesized from $Ti(OC_3H_7)_4$ of different dilutions was characterised using (a) X-ray analysis, (b) chemical analysis, (c) DTA and TGA, and (d) Electron microscopy.

3.1.1 <u>X-ray diffraction studies</u> : X-ray diffraction patterns of the synthesized samples were obtained with CuK_α radiation with Ni filter, at 500 cps and at a scanning rate of 2° (2θ)/minute on GE-XRD-6 diffractometer. The X-ray diffraction machine was set to a tube voltage of 45 kV, tube current of 15 mA and time constant of 4 seconds. The same conditions were used through out this work. X-ray diffraction studies were also made on the above samples calcined at $200^\circ C$, $600^\circ C$, $800^\circ C$, $1000^\circ C$ and $1200^\circ C$ for 4 hours.

3.1.2 <u>Results and discussion</u> : $BaTiO_3$ has a perovskite structure (Fig. 5) which will be cubic above $120^\circ C$ (Curie temperature) and on cooling below $120^\circ C$ it assumes a tetragonal structure with $a_o = 3.994$ and $c_o = 4.038$. Anliker et al. [24] in their investigation on fine $BaTiO_3$ particles, have shown that ferroelectric properties decrease
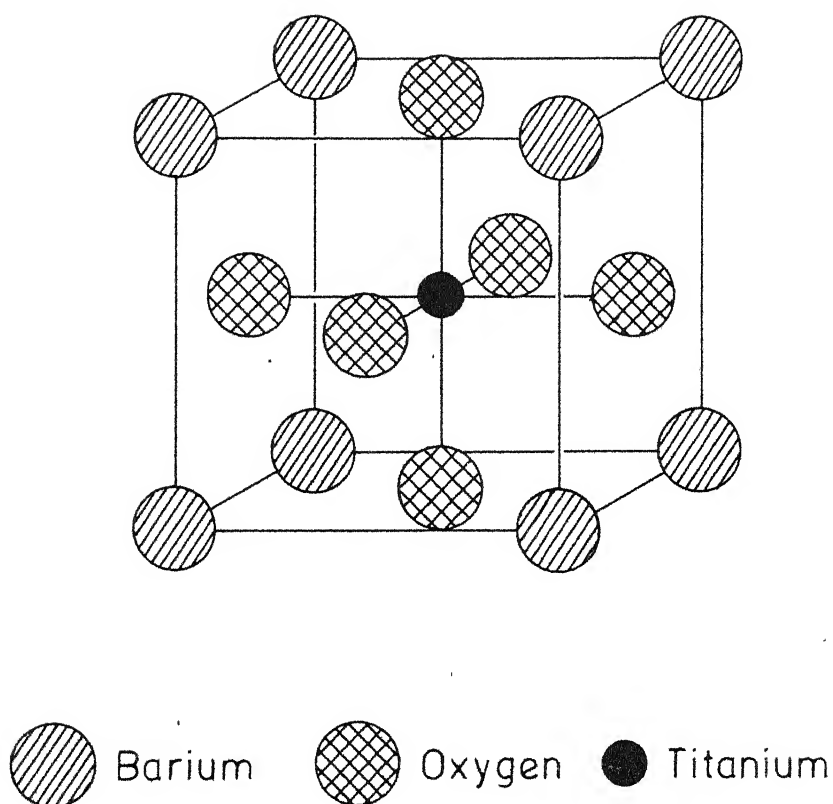
Fig. 5 The perovskite structure as typified by BaTiO$_3$ above its Curie point.

with decrease in crystal size and transition from polarised tetragonal to unpolarised cubic structure spreads over a wide temperature range instead of sharp Curie point and this spread increased with decrease in particle size. They also found that c/a ratio of fine $BaTiO_3$ decreased with decrease in particle size ($\cdot$ 4μ). From electron diffraction studies they found that the deviation from the normal behaviour takes place because of a surface layer of about 100 $\overset{\circ}{A}$. Spontaneous strain (c/a-1) in this layer seemed to be more than the volume average of spontaneous strain found by X-ray method. This misfit between surface layer and interior region causes broadening of transition region and lattice distortion resulting in X-ray line broadening. In their X-ray diffraction studies on $BaTiO_3$ of different particle sizes, upto 4μ the diffraction peaks were well resolved indicating the tetragonality. But below this size, the peaks were not resolved and appeared broad.

In the present investigation, on analysing the results obtained from X-ray diffraction studies of different samples, it was found that the as synthesized samples have a cubic structure with lattice parameter 4.034 $\overset{\circ}{A}$ (Fig. 6b). This was determined by extrapolation method of Nelson and Riley using the function, $\frac{1}{2} [\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}]$. The effect of dilution of $Ti(OC_3H_7)_4$ on the crystallinity of $BaTiO_3$ is apparent in Fig. 6(a). Lattice parameter was not calculated

Fig. 6(a) aTiO₃.

Lattice parameter a in Å

$$\frac{1}{2}\left[\left(\frac{Cos^2\theta}{Sin\theta}\right)+\frac{Cos^2\theta}{\theta}\right]$$
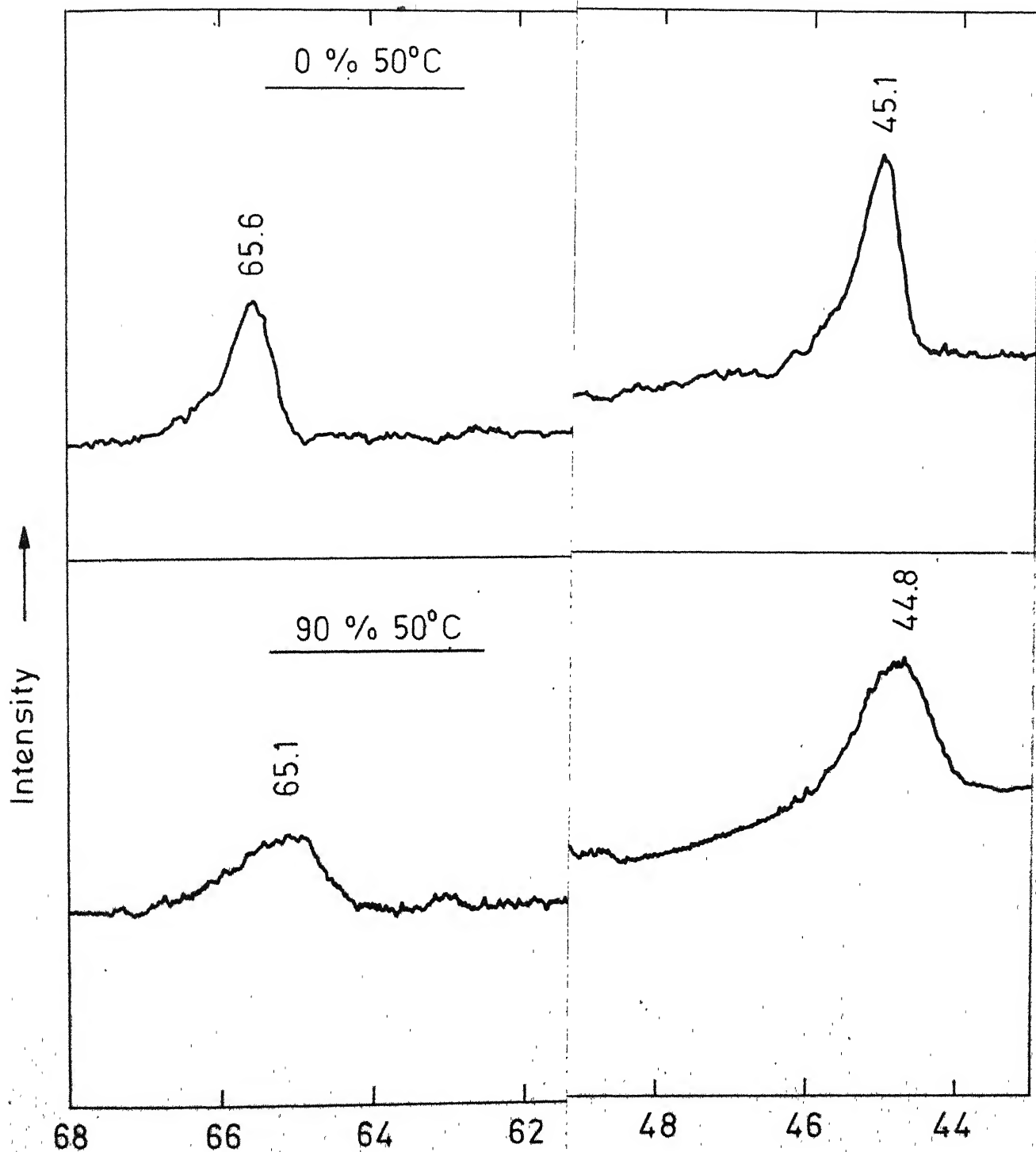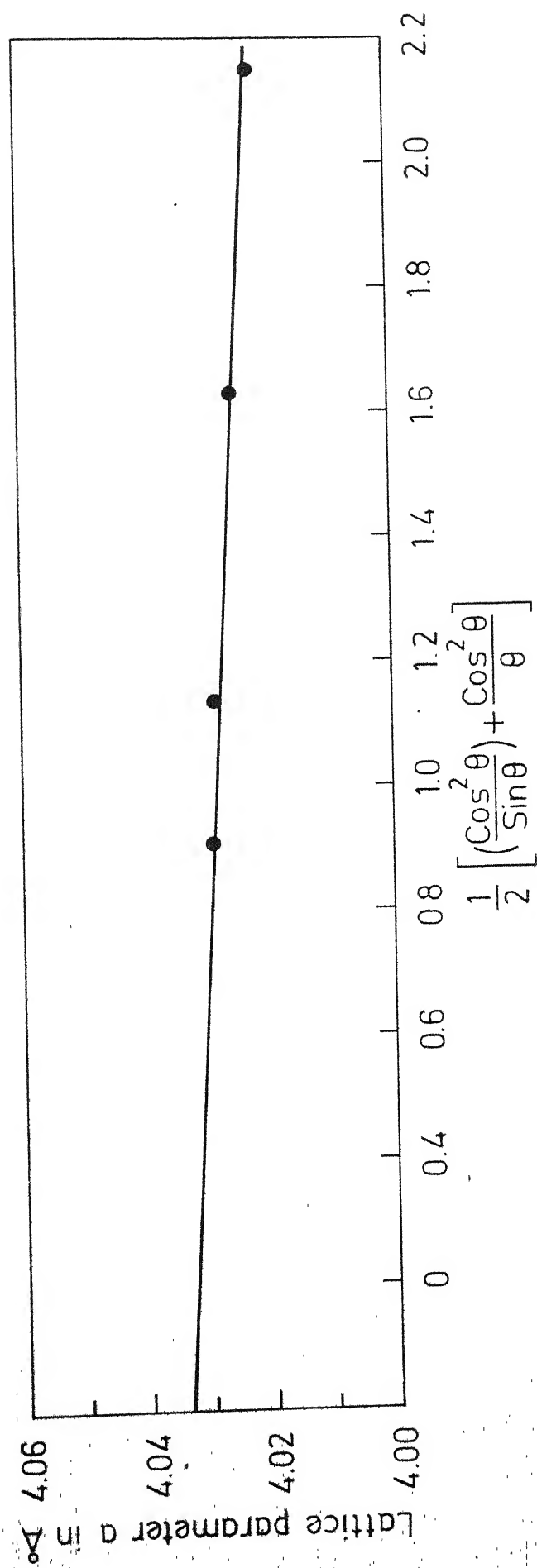
Fig. 6(b)   Lattice parameter calculation of cubic BaTiO$_3$ (0 %, 50°C)

for 90% 50°C sample because of its low crystallinity. Only
0% 50°C and 90% 50°C are given in Fig. 6(a) as the patterns
of 0% 50°C, 25% 50°C and 50% 50°C samples were alike. It
can be noticed that the peaks are well defined for 0% 50°C
sample, where as the line broadening is clearly evident in
90% 50°C sample.

Calcination at higher temperature resulted in lattice
shrinkage and higher crystallinity. Hyatt et al. [14]
mention that the character of 002 and 200 reflections give
a qualitative degree of tetragonality. For coarse grain
powder these two reflections will be resolved and for fine
grained powder these will not be resolved and instead of this
a broad peak corresponding to 200 observed. Line broadening
due to particle size obscures this 002 peak, but the peak
becomes asymmetric. This was found to be true in the present
case also as can be seen in fig. 7. There was no resolution
of the peaks even after heating the samples upto 1200°C.
This shows that the particles have not grown enough to
indicate tetragonality even at 1200°C. The lattice para-
meters calculated for samples calcined at different temp-
erature assuming a cubic structure show a considerable lattice
shrinkage which might be due to increased crystallinity.
The observed results are in close agreement with Mazdiyasani's
result as can be seen in table 2.

Table 2 - Comparison of X-ray data

ASTM data for Tetragonal BaTiO₃			Masayasani's [18] data for alkoxy derived BaTiO₃				Present data			
			as synthesised		Calcined at 700°C for 4 hrs		As synthesised 0% 53°C		Calcined at 800°C for 4 hrs	
d in Å	I	hkl	d in Å	I	d in Å	I	d in Å	I	d in Å	I
4.03	12	001	4.022	VW	4.02	VW	4.0187	W	4.0187	W
3.99	25	100	3.952	VW	3.970	W				
2.838	100	101	2.836	VS	2.814	VS	2.8376	VS	2.8244	VS
2.825		110								
2.314	46	111	2.315	S	2.301	S	2.3189	S	2.3075	S
2.019	12	002	2.013	S	1.998	S	2.011	S	1.996	S
1.997	37	200								
1.802	6	102	1.797	W	1.784	W	1.797	W	1.789	W
1.790	8	201								
1.642	15	112	1.645	S	1.629	S	1.646	S	1.650	S
1.634	35	211								
1.419	12	202	1.418	W	1.412	S	1.4219	S	1.4116	S
1.412	10	220								
1.337	5	212	1.340	VW	1.328	W	1.3412	VW	1.3513	W
1.332	2	221								
1.275	5	103	1.270	VW	1.263	S	1.2725	VW	1.2624	S
1.264	7	301								
1.263	9	310								
1.214	3	113	1.209	VW	1.204	W	1.2148	VW	1.2046	W
1.205	5	311								

Table 2 (...Contd.)

ASTM data for Tetragonal BaTiO₃			Nadaayasani's [18] data for alkoxy derived BaTiO₃				Present data			
			as synthesised		Calcined at 700°C for 4 hrs		as synthesised 0% 500C		Calcined at 800°C for 4 hrs	
d in Å	I	hkl	d in Å	I	d in Å	I	d in Å	I	d in Å	I
1.1569	7	222	1.1715	VW	1.1532	W	—	—	—	—
1.1194	1	203	1.1133	VW	1.1072	VW	—	—	—	—
1.1161	1	302								
1.0746	7	213	1.0767	W	1.0690	S	—	—	—	—
1.0703	12	312								
1.0679	12	321								

Following conclusions can be drawn from the X-ray studies of synthesized $BaTiO_3$ sample.

(a)   Increased dilution of $Ti(OC_3H_7)_4$ decreases the crystallinity of $BaTiO_3$

(b)   Because of the low particle size tetragonality of the sample is very low as indicated by the diffraction peaks.

(c)   Calcination at high temperature results in increased crystallinity.

3.2   Determination of Ba/Ti ratio by Chemical Analysis

Quantitative chemical analysis was conducted on the synthesized samples to find the deviation from the stoichiometry using the method adopted by Claunbaugh et al. [17].

Procedure :   250 mg of $BaTiO_3$ was weighed in a balance (Mettler) to the accuracy of 0.0001 gm.   7.5 ml of concentrated HCl was added to this powder taken in a 250 ml beaker and gently heated.   To this solution 7.5 ml of distilled water was added and the whole solution was boiled till the $BaTiO_3$ sample completely dissolved in the acid solution. This was diluted with 50 ml of distilled water and to this solution 25 ml of ethylene diamine tetra acetic acid made by dissolving 1.5 gm of the reagent in 50 ml distilled water with enough NH_4OH to effect dissolution, was added. The pH of the solution was adjusted to be between 3.5-4 using

dilute NH_4OH. The resulting solution was heated to boiling and Ba was precipitated as $BaSO_4$ by adding 10 ml of 25% $(NH_4)_2SO_4$ solution (aqueous). This much sulphate is necessary to precipitate Ba at pH 3.5-4, in presence of complexing agents. This solution was boiled till $BaSO_4$ settled down and the liquid above became clear.

The precipitate was removed by filtration using Whatman 40 ash-less filter paper and ignited at $800^{\circ}C$ for 3 hours and finally weighed as $BaSO_4$. The amount of BaO was calculated from this.

The combined filtrate and washings were acedified with 10 ml of concentrated H_2SO_4. The resulting solution was cooled to $10^{\circ}C$ and Ti was precipitated using 6% aqueous solution of Cupferron. The precipitate was ignited and weighed as TiO_2. The results of the analysis are given in Table 3.

Table 3 — Results of chemical Analysis

Sample No.	Weight of $BaSO_4$ in mg	Weight of BaO in mg	Weight of TiO_2	Ratio of BaO/TiO_2
1	252	165.74	85	1.015
2	252	165.74	84.5	1.02
3	252	165.74	85	1.015

Discussion : EDTA is necessary in the analytical separation of Ba and Ti because in the absence of EDTA, $BaSO_4$ gets contaminated with Ti as observed by spectrochemical analysis [17]. [Claubaugh et al found that Ti/Ba ratio was 0.991 in the absence of EDTA, whereas it was 1.000 in its presence.]

Cupferron is the ammonium salt of N nitroso N phenyl hydroxyl amine. This forms insoluble compound with Ti in strongly acedic solution (5-10 H_2SO_4 or HCl). It is employed as 6% aqueous solution. This should be freshly prepared, since it does not remain satisfactorily for more than few days. Precipitation is carried out in cold as cupferron decomposes into nitrosobenzene on heating. Initially a curdy precipitate forms till all Ti is precipitated and later needle like flocculant precipitate of free nitroso phenyl hydroxyl amine is formed. This should be filtered as soon after their formation as possible since excess cupferron is not very stable in acedic solution. Ignition of the precipitate has to be done gradually and carefully in a large crucible to avoid mechanical losses by gaseous compounds.

A qualitative observation made by Claubaugh et al was that when Ti content exceeded significantly from the stoichiometric ratio, the resulting $BaTiO_3$ did not dissolve completely. This can be considered as a rapid means of indicating excess of Ti.

From the results of the analysis we see that the synthesized $BaTiO_3$ is very close to stoichiometric $BaTiO_3$, but with slight excess in Ba which might be due to adsorption of Ba^{++} ion on precipitated $BaTiO_3$.

3.5 Results of DTA, TGA

Upon action of heat most compounds undergo certain specific chemical and physical transformation accompanied by thermal processes like evolution and absorption of heat. Weight and morphological properties are also changed.

DTA and TGA of $BaTiO_3$ samples were conducted on a derivatograph (MOM Budapest) from $25^\circ C$ to $1000^\circ C$, at a heating rate of $10^\circ C/min$, in ambient atmosphere. Specifically 25% $50^\circ C$, 90% $50^\circ C$ and 90% $400^\circ C$ were chosen for DTA studies. A significant exothermic peak appeared in range of $400^\circ C$ (8(a), 8(b)). It can be recalled that in X-ray studies, there was lattice shrinkage in the calcined samples compared to as synthesized $BaTiO_3$. Moreover, it is apparent that this peak is very weak in the 90% $400^\circ C$ (8c) sample. From these considerations, we can attribute this peak to the process where fine as synthesized $BaTiO_3$ particles grew with the reduction in surface energy, at the same time getting more crystalline, as seen by the lattice shrinkage. Calcined powder which had already gone through this process, naturally showed a very weak peak in this range.
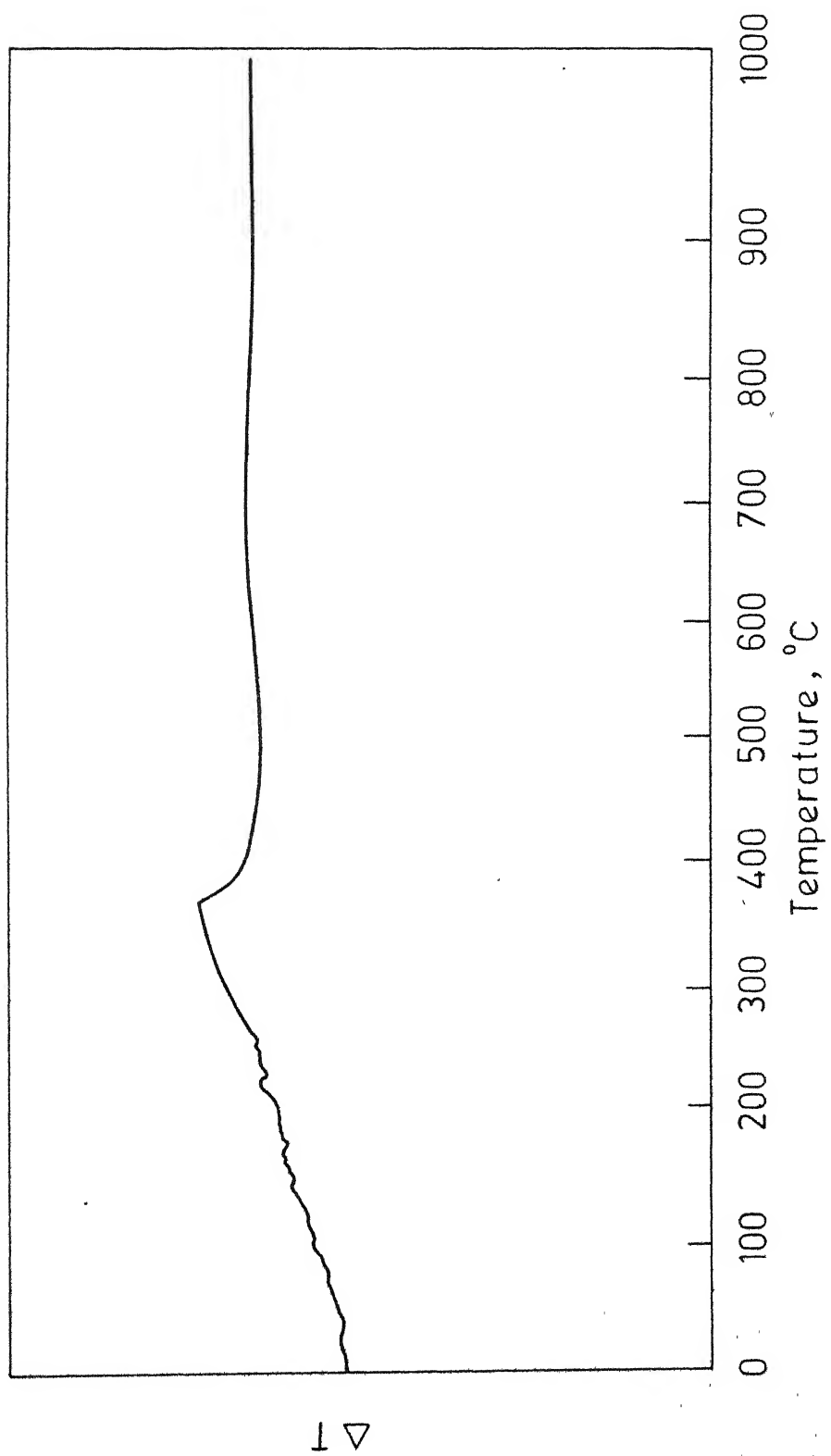
Fig. 8(a) DTA of BaTiO₃ (25 %, 50°C sample).

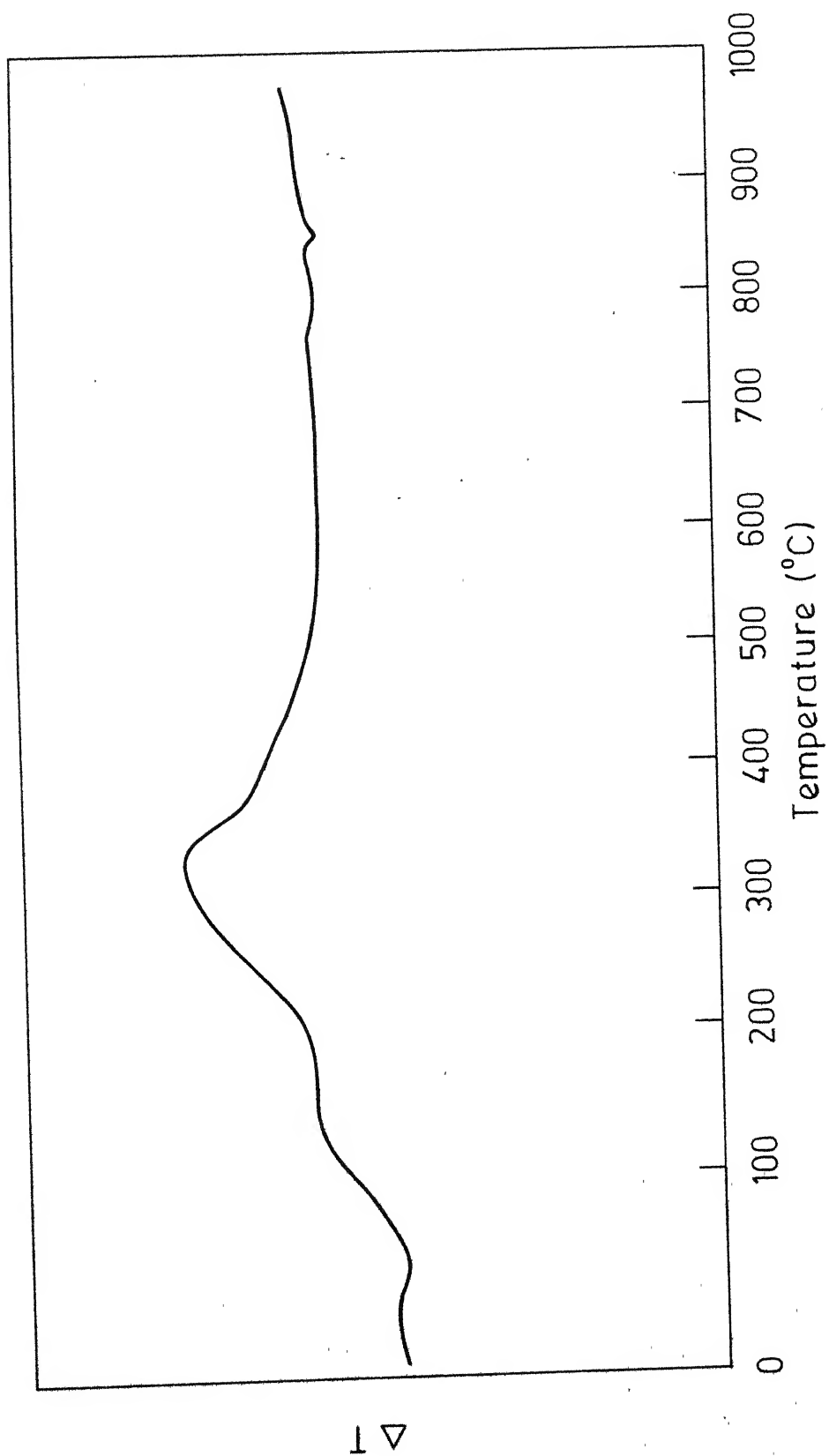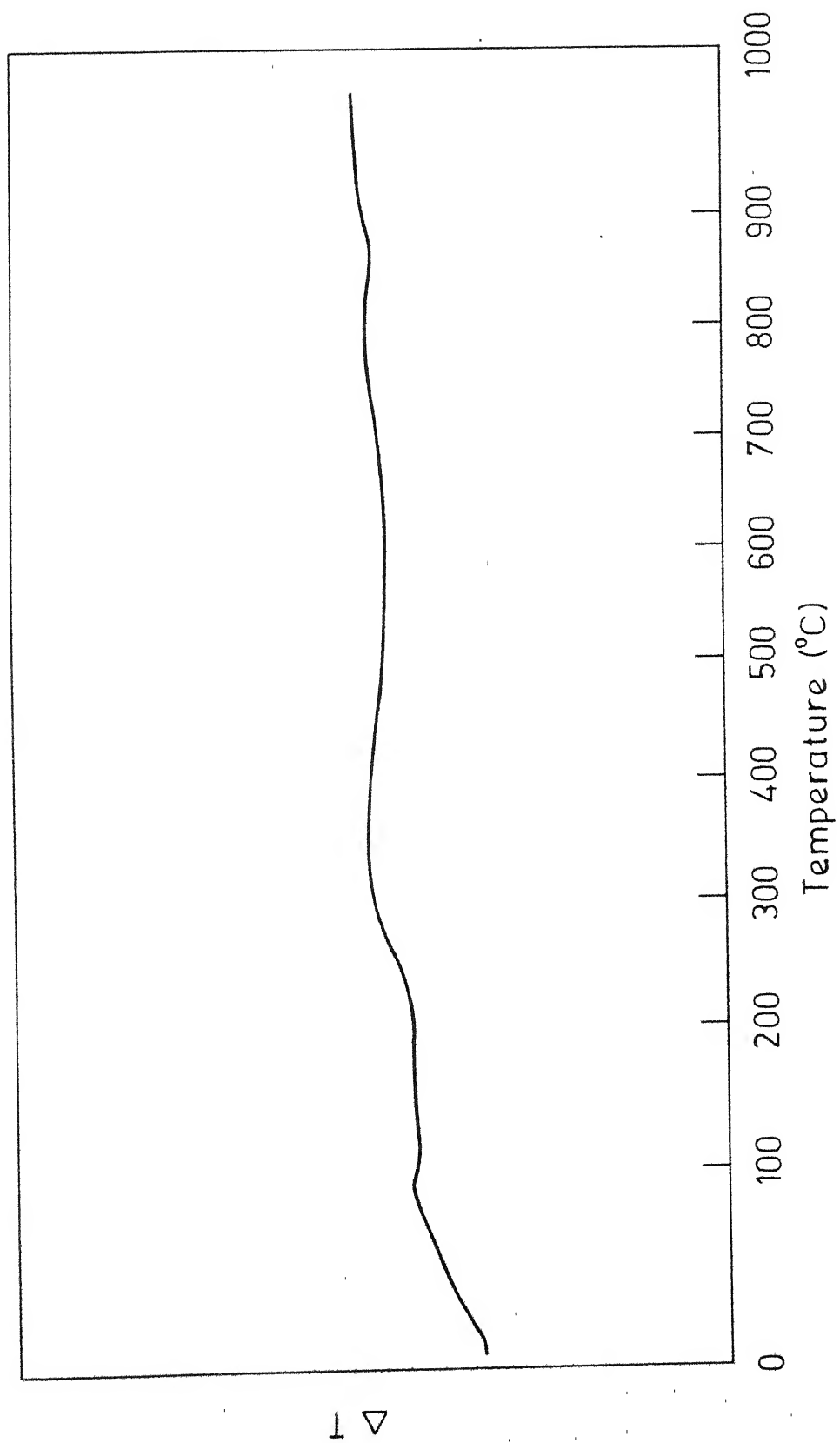Fig. 8(b) DTA of $BaTiO_3$ (90 %, 50°C sample)

Fig. 8(c)   DTA of BaTiO$_3$ (90 %, 400°C (2 hrs) sample).

Thermogravimetric analysis showed a loss of 10 wt%(Fig.8d) in 25/ 50°C sample 15 wt/ in 90/ 50°C samples at 1000°C which can be attributed to removal of bound alcohol, CO_2 and moisture. 10/ loss in weight is very common in the powders synthesized by organometallic method. Inspite of drying the powder in He atmosphere, Mazdiyasani found 10% loss in weight at 900°C in the synthesized $BaTiO_3$ [18].

3.4 Electron Microscopic Studies

Electron microscopy is a powerful tool in the characterisation of ultrafine ceramic powders. In the present work particle size distribution and shape characteristics of both as synthesised samples and samples calcined at 800°C were studied using Philips EM 301 electron microscope.

1-2 mg of sample was taken in a very clean test tube. 5-6 ml of ethyl alcohol was added to this. Particles were dispersed in ethyl alcohol by holding the test tube in an ultrasonic bath for about 10 minutes. If the resultant suspension looked whitish, some more alcohol was added till it appeared almost colourless and again held in ultrasonic bath for 5 more minutes. A drop of this suspension was placed on a carbon film supported over 200 mesh copper grid. Even then agglomerates could not be removed fully, but the resolution between the particles were good enough to carry out size measurements. Number of electron micrographs were taken in for all the samples. Electron diffraction patterns
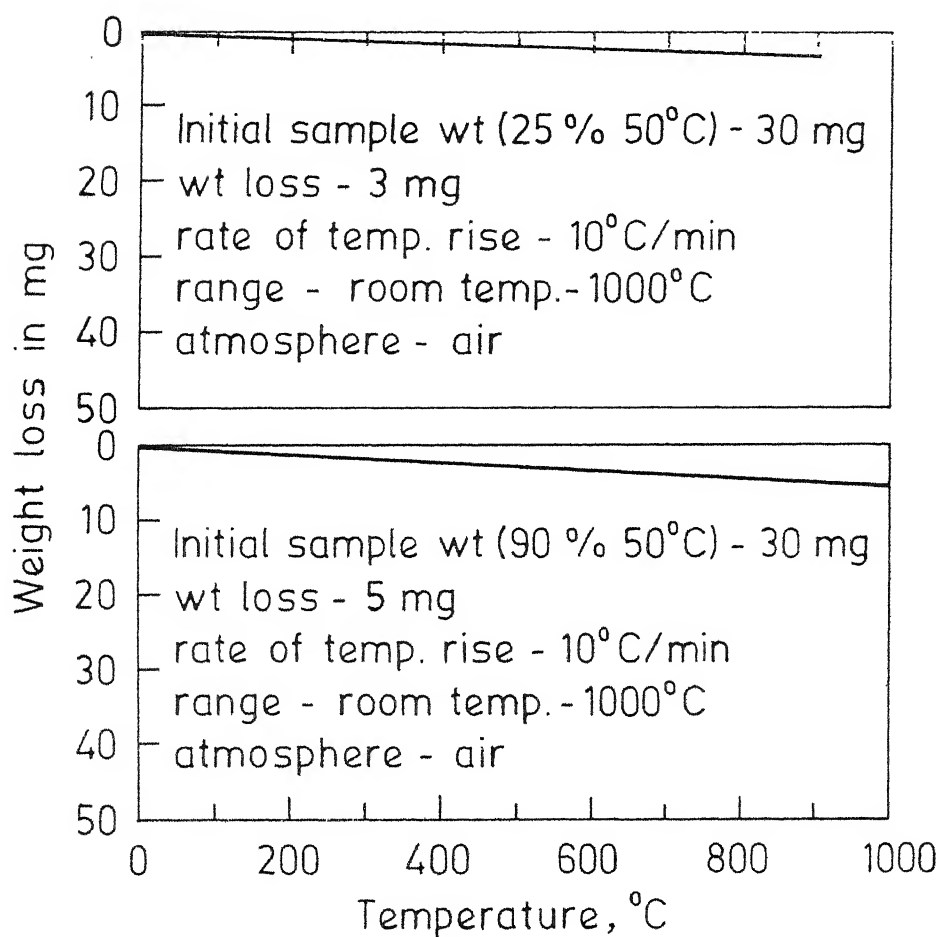
Fig. 8(d)   TGA of BaTiO$_3$ samples.

of these samples were also taken. Cumulative size distribution of particles for each sample was plotted after counting 100 to 150 resolved particles for each sample. The plots are given in fig10-13. It is evident that for as synthesized samples, the size distribution is narrow and the particle size has increased considerably for the calcined samples. The electron micrographs of the above samples are given in figures 9(a)-9(d).   From the micrograph, we can clearly see the change in the particle shape after calcination. Most of the particles in calcined samples have taken symmetric regular shapes. The increase in particle size after calcination clearly supports the results of DTA studies.

Kiss et al [22] observed a systematic decrease in particle size of $BaTiO_3$ with the increased dilution of titanium alkoxide. In the present investigation such regular decrease was not observed. This might be because of the following factors. The alkoxide used by them for $BaTiO_3$ synthesis was a chelate of $Ti(OC_3H_7)_4$ having a considerably slower hydrolysis rate as compared to $Ti(OC_3H_7)_4$. In the case of $Ti(OC_3H_7)_4$ because of its high hydrolysis rate, the lower dilutions does not seem to affect the particle size of $BaTiO_3$ much, though at very high dilution like 90%, there has been a decrease in particle size along with crystallinity.

Fig. 9(a)1 Electron micrograph of о 50°C BaTiO₃ sample
scale 1 cm = 950 Å.

Fig. 9(a)2 Electron micrograph of о 50°C sample calcined
at 800°C (4 h), scale 1 cm = 950 Å.

Fig. 9(b)1   Electron micrograph of 25%, 50°C sample
              scale 1 cm = 700 Å.

Fig. 9(b)2   Electron micrograph of 25% 50°C sample calcined
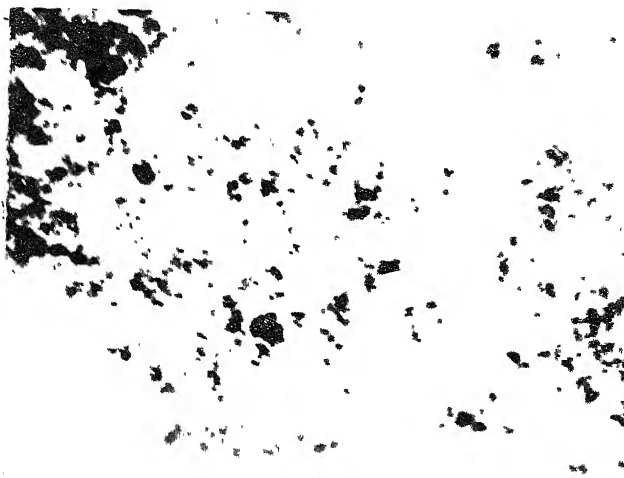   at 800°C (4h)
              scale 1 cm = 1450 Å.

Fig. 9(c)1   Electron micrograph of 50 : 50°C sample
              scale 1 cm = 1700 Å.

ig. 9(c)2   Electron micrograph of 50 : 50°C sample calcined
             at 800°C (4h)
             scale 1 cm = 700 Å.

Fig. 9(a)1   Electron micrograph of 90 50°C sample
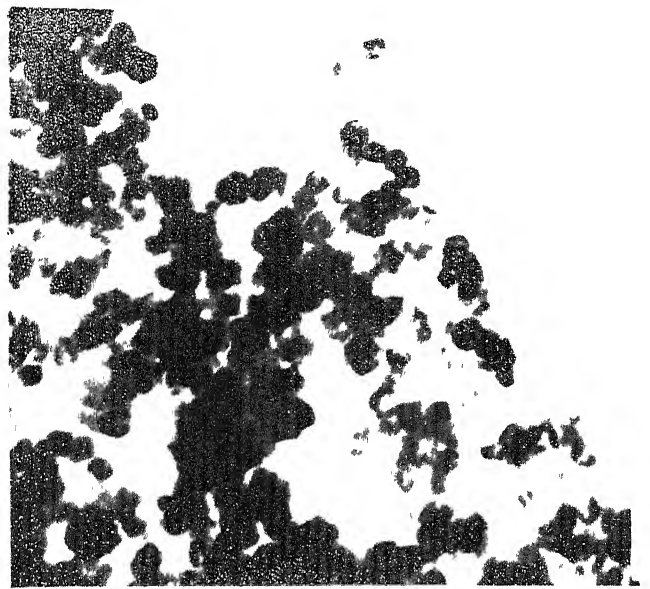   scale 1 cm = 950 Å.

Fig. 9(d)2   Electron micrograph of 90/50°C sample calcined
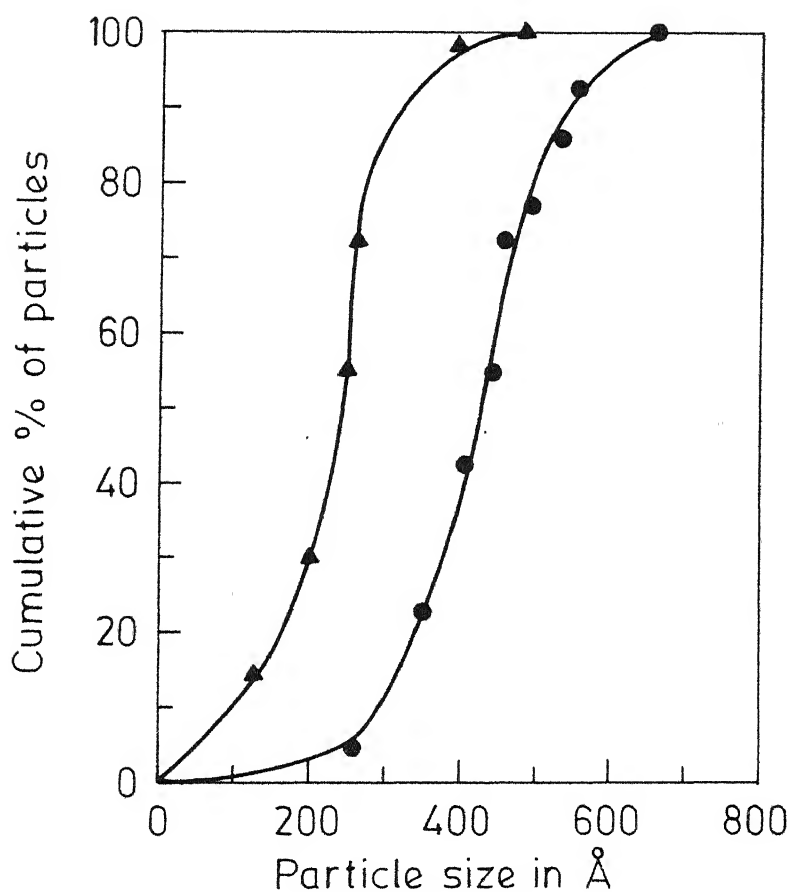   at 800°C (4h)
              scale 1 cm = 950 Å.

Fig. 10 Cumulative size distribution of 0 % BaTiO₃ samples.

▲ 50°C, average particle size 275 Å
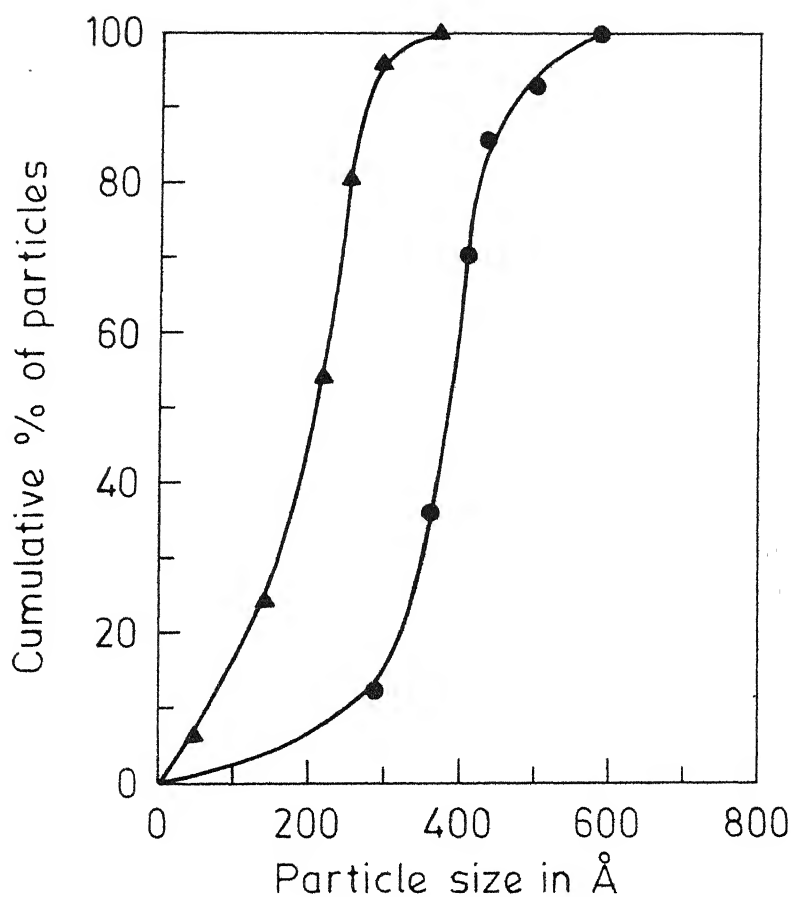● 800°C (4 hrs), average particle size 440 Å

Fig. 11 Cumulative size distribution of 25 % BaTiO$_3$
samples.
▲ 50° C, average particle size 240 Å
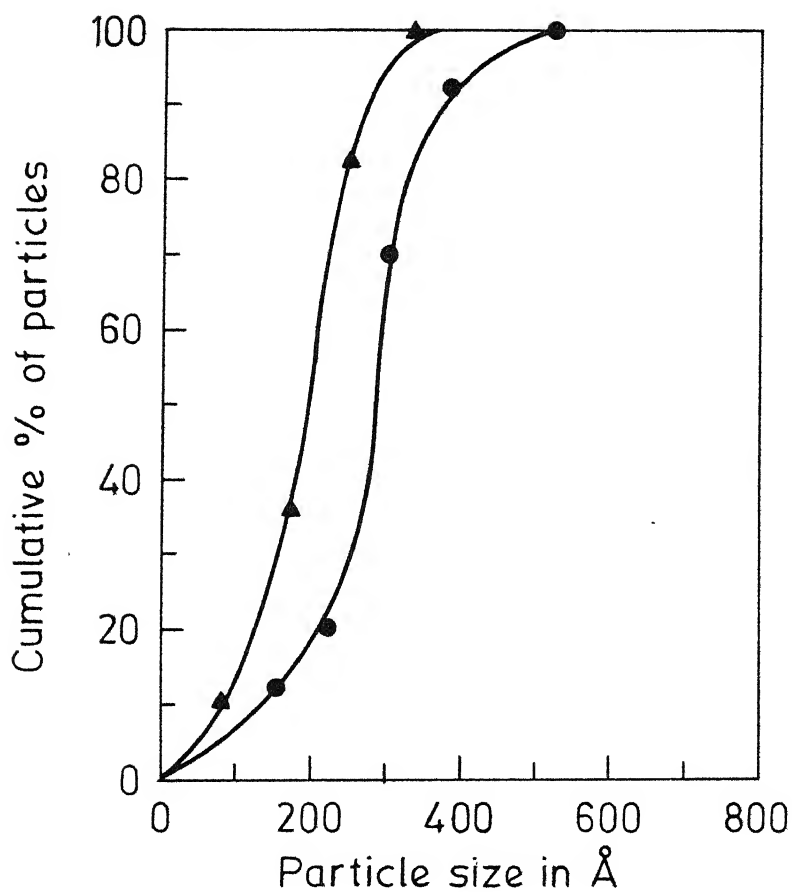● 800° C (4 hrs), average particle size 410 Å

Fig. 12 Cumulative size distribution of 50 % BaTiO$_3$ samples.

▲ 50°C, averag particle size 230 Å
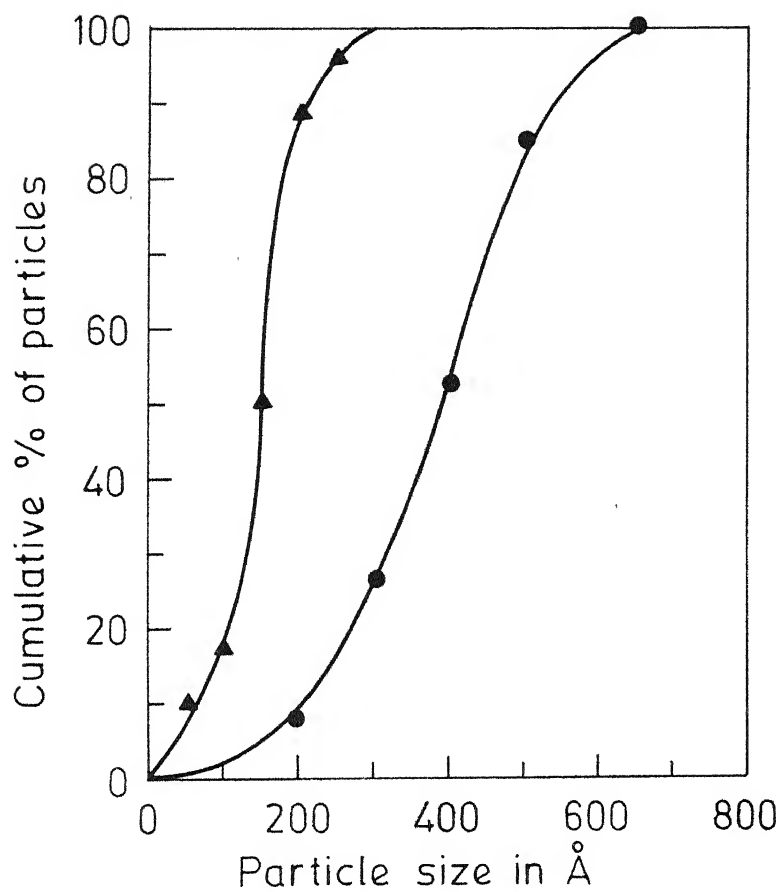● 800°C (4 hrs), average particle size 350 Å

Fig. 13 Cumulative size distribution of 90 %
BaTiO₃ samples.
▲ 50°C, average particle size 190 Å
● 800°C (4 hrs), average particle size 490 Å

Chapter 4

SINTERING AND MICROSTRUCTURAL STUDIES

Abstract : Synthesized $BaTiO_3$ samples were pelletised and sintered at both $1250^{\circ}C$ and $1300^{\circ}C$ for one hour and two hours. The densities of these sintered pellets were evaluated and microstructure was studied using metallographic technique.

4.1 Pelletisation

$BaTiO_3$ powder used for sintering studies was calcined at $800^{\circ}C$ for one hour to remove the adsorbed gases. It is not advisable to use the as synthesized powder for sintering because of the considerable quantity of adsorbed gases in such powder. These adsorbed gases, if not eliminated, may affect the final density of the material.

The calcined powder was mixed thoroughly with about 5% of polyvinyl alcohol (PVA). This PVA was prepared by dissolving 20 gms of PVA powder in 100 ml of hot distilled water. The powder was pressed into thin cylindrical pellets of thickness between 0.5-0.6 mm in a 3/8" diameter split die. Pressing was done in a hydraulic press (Carver laboratory press, Model B), pressing force was 10,000 psi.

The dimensions of the green pellets were measured using a micrometer (least count 0.001 cm). The green

densities of these pellets were evaluated by finding their mass and volume. Green densities of the pellets were found to be between 50 to 55 of theoretical density (6.02 gm/cc for tetragonal $BaTiO_3$).

4.2 Sintering

A bed of pure zirconia (99) was spread on a fire brick slab and the green pellets were placed on it. Sintering was carried out in a silicon carbide tube furnace which had a central four inches constant temperature zone. Heating rate was approximately $200^{o}C$/hour and cooling rate much faster, i.e. approximately $300^{o}C$/hour. Sintering was conducted at two temperatures $1250^{o}C$ and $1300^{o}C$ for period of one hour and two hours. The temperature was to a accuracy of $\pm10^{o}C$.

4.3 Density Measurements

Densities of the fired pellets were measured using Archimede's principle. The dry weight D of the pellet was found in a balance (Mettler, accuracy 0.0001 gm). These pellets were hung in a beaker containing distilled water. This was boiled for 5 to 6 hours and left in water for 4-6 hours. Then the water suspended weight 'S' and the water saturated weight W of the pellets were determined. The density 'ρ' was evaluated using the formula, $\rho = \frac{D}{W-S}$. The density values at different sintering temperatures are reported in table 4.

Table 4 - Density and linear shrinkage of sintered BaTiO$_3$
pellets

Sintering temperature in $^{\circ}$C	Sintering time in hours	Linear shrinkage in percentage	Density in gm/cc	Percentage of theoretical density[*]
1250	1	23.5	5.56	92.3
1250	2	23.5	5.70	94.7
1300	1	23.4	5.68	94.3
1300	2	24.1	5.72	95.0

[*]Theoretical density of tetragonal BaTiO$_3$ = 6.02 gm/cc.

4.4 Microstructure

Microstructure of $BaTiO_3$ is very sensitive to deviation from stoichiometry. An excess of 2 Ba (mole) gives a fine grained $BaTiO_3$ (5-10μ), whereas an excess of even 1 Ti results in enormous grain growth giving coarse textured ceramic of grain size 50-100μ or larger [25].

In the present investigation microstructures of the sintered pellets were observed by ordinary metallographic techniques developed by Kulscar [26]. Pellets were polished on 2/0, 3/0 and 4/0 emergy papers by rubbing the pellet on the paper in a circular motion. Kerosene was used as the lubricant during this part. Final polishing was done on a cloth wheel using 0.3μ alumina particles suspended in distilled water as the abrasive. There were lot of 'pull outs' from the polished surface of the pellets when polished on a cloth wheel. This could not be avoided because of the relative softness of $BaTiO_3$ ceramic to such abrasion. This is reflected as black spots in the microstructure, which should not be confused as second phase. The absence of any second phase was verified by studying the X-ray diffraction pattern of the sintered pellets.

After polishing, the pellets were etched with an etchant consisting of 10% HCl (10 ml HCl in 100 ml water) and 20 drops of 50% HF. Etching time of 1-1½ minutes was

sufficient to reveal the grain structure. With deeper etching of 3-4 minutes, the domain structure was visible. The microstructure of samples sintered at 1300°C for 2 hrs is given in Fig. (15a). The grain size of this determined by linear intercept method was found to be 15μ.

The photomicrographs of domains observed in larger grains are given in fig. (15b) and fig. (15c). The domain structure which is in the form of series of parallel lines result from an alteration between two positions of c axis approximately 90° apart (90° domains). Since the texture of domains are very fine, very high resolution is necessary to observe them clearly. Because of this limitation in the microscope, the domains appear faintly in the micrograph. The room temperature dielectric constant and loss were measured after electroding the sample, in a capacitance bridge (GRC Type 1615-A). Electroding was done by applying fired on silver paint to the pellets in circular shape on both sides of the pellet coaxially and then fired at 750°C for $\frac{1}{2}$ hour. The value of room temperature dielectric constant and loss angle are given in table 5.

The plots of dielectric constant vs temperature are given in fig. (14) for 1250/2 hr and 1300/2 hr samples. For normal $BaTiO_3$ ceramics, this plot gives a very high value of dielectric constants at Curie temperature of 120°C. However, in the present plot we observe just a nominal increase in dielectric constant around Curie

Table 5 – Properties of $BaTiO_3$ ceramics based on powder synthesized by the hydrolysis of $Ti(OC_3H_7)_4$ in $Ba(OH)_2$ solution

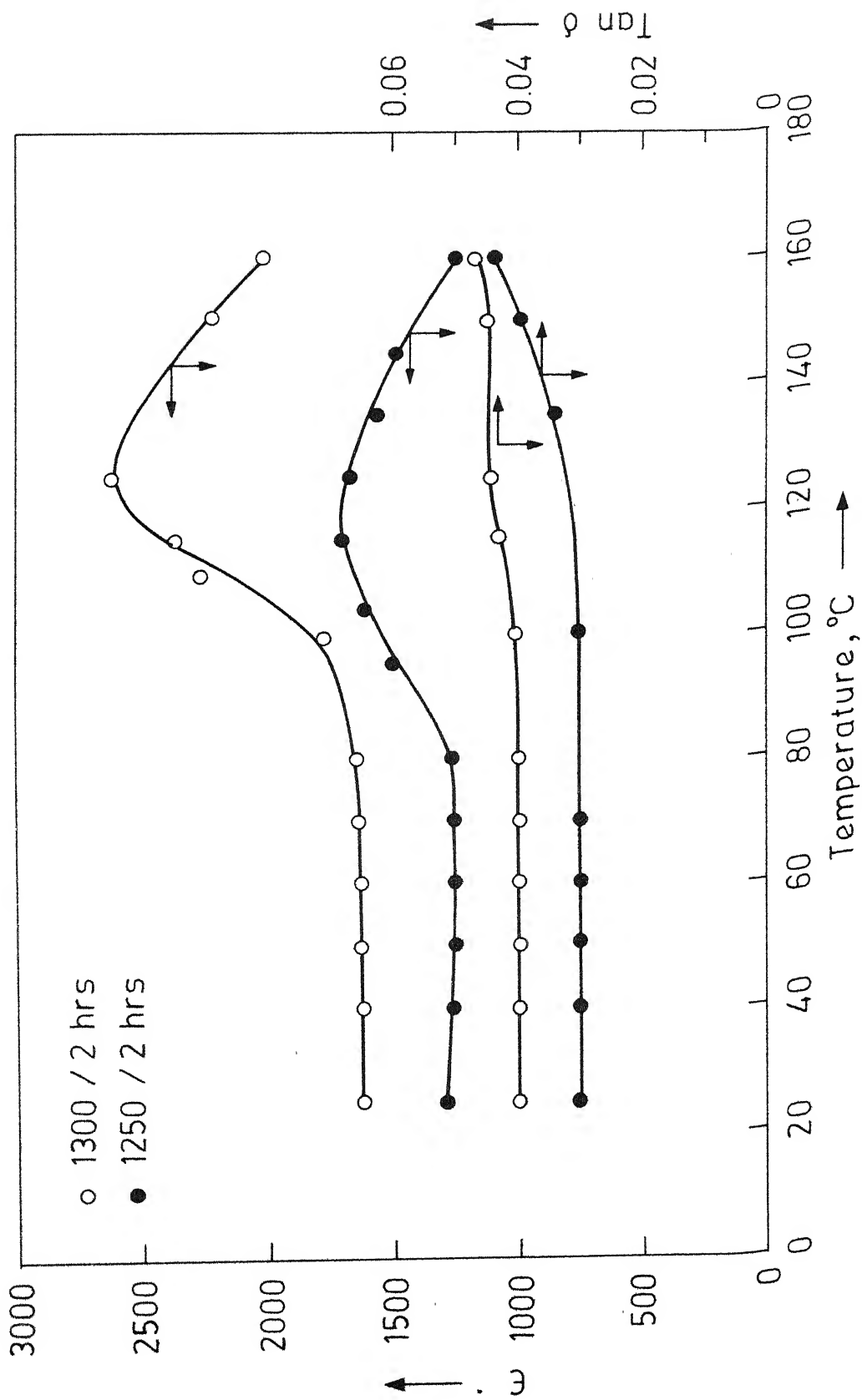| Sample	Dielectric constant ε	Loss
1250/1 hr	1350	0.03
1250/2 hr	1298	0.04
1300/1 hr	1660	0.036
1300/2 hr	1758	0.05

Fig.14 ϵ and tan δ vs T plot of sintered $BaTiO_3$ ceramics.

Fig. 15(a)   Photo micrograph of BaTiO₃ ceramic sintered at
             1300°C for 2 hr.
             scale = 1 cm = 20μ.

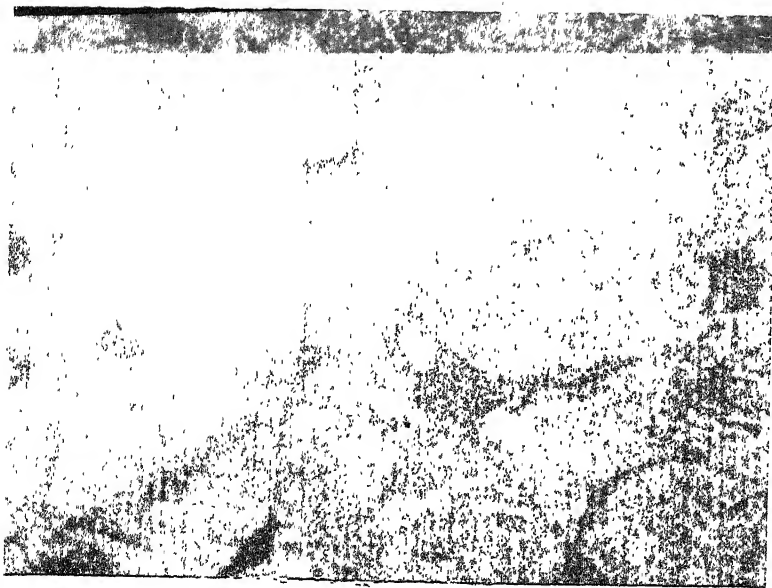Fig. 15(b)   Domain structure in BaTiO₃ ceramic sintered
and   15(c)   at 1300°C for 2 hrs.
               scale 1 cm = 10µ.

temperature. Ainger et al. [27] observed that BaTiO$_3$
ceramics having a imperfect tetragonal structure, with very
low c/a ratio ao not show a sharp increase in aielectric
constant at Curie temperature. In the present case, the
X-ray aiffraction stuaies of sintered BaTiO$_3$ samples aia
not show any resolution in the diffraction peaks charac-
teristic of tetragonal moaification, though there was
asymmetry in certain diffraction peaks. From this observa-
tion, we can say that the absence of high aielectric
constant peak at Curie temperature in the samples investi-
gated might be aue to the fact that the sintered samples
have a imperfect tetragonal structure (low c/a ratio). But
further experiments are necessary to fully confirm this.

CONCLUSIONS

(a)   Stoichiometric ultrafine $BaTiO_3$ ceramic powder can be synthesized by the hydrolysis of $Ti(OC_3H_7)_4$ in a high pH (13) $Ba(OH)_2$ solution.

(b)   Use of highly diluted $Ti(OC_3H_7)_4$ for the synthesis reduces the particle size and crystallinity of $BaTiO_3$ as apparent from x-ray studies.

(c)   Calcining the powder at higher temperature results in lattice shrinkage and increased crystallinity.

As synthesised powder has the cubic modification, on calcination above $1000^{\circ}C$ shows a tetragonality as observed in the asymmetry of certain x-ray diffraction peaks.

(d)   DTA of as synthesized $BaTiO_3$ gives a prominent exothermic peak in the $400^{\circ}C$ range. This peak is very weak in the calcined material, which indicates that exothermic peak should be associated with the process in which particles tend to grow and reduce their surface area. The growth of particles with calcination is evident in particle size distribution studies made with help of electron microscope. Calcined samples apart from having increased size also show a definite symmetry in their shapes.

(e)   TGA of as synthesized samples show a weight loss of
        10-15 which is due to the removal of moisture,
        adsorbed gases and bound alcohol.

(f)   The synthesized ultrafine powder can be sintered to
        densities 95% of theoretical density at temperature
        as low $1250^{\circ}C$ which is almost $100^{\circ}C$ less than that
        required for conventional materials.

(g)   The $BaTiO_3$ ceramic samples sintered at $1250^{\circ}C$ and
        $1300^{\circ}C$ in the present case appear to have a low c/a
        ratio as observed by x-ray diffraction pattern and
        the ε-T plot. It would be interesting to conduct
        further experiments to study this low tetragonality
        behaviour.

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